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ELECTRODE PASSIVATION STUDIES

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Air Force Aero Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

NOTICES

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FOREWORD

This report was prepared by Tyco Laboratories, Incorporated, Waltham, Massachusetts, under Contract No. AF 33(615)-3433. This contract was initiated under Project No. 8173, "Electrochemical Energy Conversion", Task No. 8173-04.

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Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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Donald P. Mortel, Acting Chief
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ABSTRACT

The operation of primary, reserve batteries in a passive mode is discussed. Anodic passivation of reactive metals, such as Zn, Fe, etc., occurs at critical currents which are of the order of 0.1 to 1 amp/cm^2. Passive anodes dissolve at current densities orders of magnitude less than the critical current. An anode can be put into the passive state by an appropriate electrical pulse and can be maintained in this condition by suitable connection to the positive battery electrode. Activation of the anode prior to use can be achieved by a cathodic electrical pulse which reduces the passive film. The activation time may be from several milliseconds to seconds, depending on the magnitude of the cathodic pulse.

The Fe and Fe-Cr systems have been examined as possible anodes in $HClO_4$ solutions. Data on passivation of these systems suggest that a Fe-5% Cr / acid electrolyte / PbO_2 reserve battery could be operated in the passive mode.

Studies of the passivation of Mg from pH 2 to 14 were carried out with a view toward using the high energy density characteristics of the Mg/m-dinitrobenzene battery. In neutral and alkaline solutions Mg is passive on open circuit and cannot be used in the passive reserve mode. A secondary passivation may be present in mildly acid fluoride solutions.

Studies of Cr, Al, and of amalgams of Mg show them to be unsuitable for use as reserve anodes.

Studies of the passivation of Zn and Zn-alloys in KOH at $30^{\circ}C$ have been made potentiostatically. Zinc shows the characteristic active-passive current-potential curve although the passive current is too high for use in the passive reserve mode in Zn-AgO batteries. Studies of the corrosion of Co, Cu, Fe, Mg, Mn, and Ti in alkaline solutions show them as possible choices for alloying with Zn to improve its standby characteristics. Cu-Zn alloys are not acceptable, however, since the addition of Cu lowers the Zn critical current but does not lower the passive current sufficiently. Zn-Mg

solid solutions show the formation of an inactive surface layer and are therefore not suitable. Cu-plating of Zn may be suitable for its protection on standby.

Studies of the passivation of Zn-Fe alloys showed them to be unsuitable: alloys of 90 Zn- 10 Fe corrode at a high rate even when passive.

Alloys of Zn-Mn have better characteristics than Zn, but the corrosion rate in the passive state is too large for the intended application.

The Zn-Co and Zn-Ni systems are promising for use as passive anodes. The active dissolution, passivation, and reactivation of passivated zinc-alloy anodes were investigated in alkaline solution varying in concentration from 1 to 6N in KOH. The 1N alkali is less aggressive than the normal battery electrolyte while 6N KOH approximates closely battery electrolytes currently in use.

Alloys of 89 Zn - 11 Co have high dissolution currents in the passive state, while the 78 Zn - 22 Co and 80 Zn - 20 Ni alloys have acceptably high critical currents and low passive currents. However, at best, the passive current is still about 5 $\mu a/cm^2$.

The activation characteristics of promising alloys were examined in some detail. The passive layer of the Zn-Ni alloy is difficult to reduce even at fairly negative potentials. However, films formed at high positive potentials can be reduced with greater ease. A series of experiments was carried out in which the passive layer was first pretreated at an anodic potential and then the electrode activated at 0.0 v. It was observed that anodic pretreatment leads to faster activation. Activation to about 75% of the original current density in the active potential region can be achieved. The Zn-Co alloys are generally activated with less difficulty than the corresponding Zn-Ni alloys.

The zinc-cobalt and zinc-nickel systems were studied in electrolytes N in KOH with additions of various salts. Electrolytes examined included $SO_4^=$, Cl^-, ClO_4^-, and F^-. In general, the behavior of these

alloys is approximately the same in N KOH and in N KOH containing the above salts. However, some changes of the passive current and of the critical current and some differences in the time dependence of the passive current were observed in solutions containing chloride salts.

A comparison of primary reserve batteries operated in the passive mode with batteries activated by conventional gas generators shows that the passive current must be less than 1 $\mu a/cm^2$ for the passive battery to be competitive. Ideally, the passive current should be less than 0.1 $\mu a/cm^2$.

Recommendations on future research on passive anodes are presented. Particular attention is given to the basic mechanisms of formation and reduction of passive films in alkaline electrolytes.

A bibliography of the literature on passivation of metals in alkaline solutions is appended.

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I. INTRODUCTION

High energy, primary batteries utilize anode materials which are highly reactive in the specific environment of the battery cell. Two principal methods have been evolved in order to extend the shelf life of these batteries. In one, the electrolyte is kept in a separate compartment and is introduced in the cell upon demand. In the other, the battery is thermally activated by a pyrotechnic compound. In this study, a third method was explored based on the active-passive transitions of reactive, anode material. The method under study would also make it possible to use reactive anodes in acid solutions and thus it would permit coupling reactive anodes to cathodes of organic depolarizers under conditions where the latter function at maximum efficiency.

a) Electrochemistry of Anode Processes

A metal anode in a primary battery undergoes oxidation according to a process which may be represented by

$$M \longrightarrow M^{z^+} + ze^-$$ (1)

or

$$M + n(OH^-) \longrightarrow M(OH)_n + ne^-$$
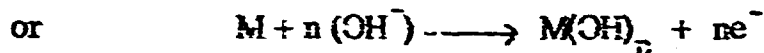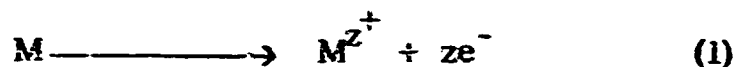
In general, this reaction occurs with some overpotential so that as its rate increases, the half-cell potential of the metal-metal ion couple becomes more positive. A battery anode material should have a low equivalent weight, a negative reversible potential, and a small overpotential for reaction (1). These characteristics are met by reactive metals, e.g., Mg, Zn, Fe, etc.

The main waste process, as far as the anode is concerned, is corrosion which occurs by combining reaction (1) with a cathodic process occurring directly on the anode. In battery operation the

anodic reaction (1) is coupled via the external circuit to the cathode, while in corrosion, it is coupled to a cathodic reaction, usually hydrogen evolution or oxygen reduction, occurring on the same electrode. It is apparent from the above, that, as a general rule, active materials corrode in the battery electrolyte; consequently, in order to get a reasonable shelf-life, we must devise ways of suppressing the corrosion reactions, at least until the battery is actually used.

A possible way of decreasing corrosion is to inhibit the cathodic process without affecting the rate of reaction (1). This can be done in certain cases, e.g., amalgamation of zinc anodes raises the hydrogen overpotential without seriously affecting the rate of anodic dissolution of Zn. However, in general, it is not possible to inhibit the rate of the cathodic corrosion reaction without also inhibiting the anodic reaction rate.

An alternative way of protecting the anode during storage is to passivate it. In this method, the anode would be maintained in the passive state until the battery was to be used, at which time the anode could be simply activated by an electrical, cathodic pulse.

b) <u>Passivation</u>

The current corresponding to reaction (1) increases generally with potential until some critical value is reached whereupon it begins to decrease. This phenomenon of negative resistance is caused by the formation, at positive potentials, of a surface oxide layer which retards the transfer of metal ions from electrode to solution. At still more positive potentials, the oxidation rate becomes independent of potential. Here, the oxidation rate is controlled by the dissolution of the surface oxide, i.e., by the rate of a purely chemical process which is not affected by the field.

The mechanism which gives rise to the potential independent portion of the current-potential curve is the following: The oxidation current at any given potential in the passive region corresponds to the rate at which metal ions leave the metal, migrate through the film, and are incorporated in the metal oxide. The rate of migration through the film is governed by the field across it, i.e., by the potential divided by the oxide thickness.

For a passive electrode in a steady-state, the rate of oxide formation equals the rate of oxide dissolution. If the potential is raised after a steady-state is achieved, oxide forms faster than it dissolves since the potential gradient across the oxide film is now greater. Consequently, the oxide thickens until the field is reduced to its previous value at which point the rate of oxide buildup and dissolution again balance each other. This process is repeated if the potential is again increased. Thus, in the passive region, the oxide increases in thickness as the potential is increased but the oxidation current remains at a constant, low value.

c) Activation

A passive electrode will revert to an active state, i.e., to one where oxidation is freely occurring, if its potential is allowed to fall below the critical passivation potentil, E_{crit}. This can be done either by removing the external bias and allowing the oxide to dissolve in the electrolyte or by reversing the bias and electro-chemically reducing the oxide. The first method is termed spontaneous activation, while the second is referred to as forced activation. Once the oxide is reduced, current can be drawn through the anode until its potential is above the critical passivation potential.

d) Application to Primary, Reserve Batteries

Application of the phenomenon of active-passive transitions to primary, reserve batteries is relatively straight-forward. Briefly, the anode is passivated during storage and is activated by a current

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pulse when power is to be delivered.

The feasibility of the proposed application arises from the relative magnitudes of the current required to passivate initially the anode, the current required to maintain it passive, and the current required to activate it.

The critical current for passivity is typically of the order of 0.1 to 1 amp/cm^2, depending on the anode material, the composition of the solution, the geometry of the electrode, and the temperature. The current required for maintain the electrode passive is typically of the order of 10^{-6} to 10^{-8} amp/cm^2, again depending on the anode material, solution composition, and temperature. The current for activation is, of course, arbitrary; its magnitude determines the time required for activation. It is shown below that currents of a few ma/cm^2 will cause activation in less than 0.1 sec.

The critical current for passivity is often substantially greater than the value given above, e.g., it is about 20 amp/cm^2 for Fe in H$_2$SO$_4$. In this case, precipitation of a non-conducting salt, e.g., FeSO$_4$ may occur at lower current densities since the salt, which is the product of anodic oxidation, is transported away from the electrode surface at rates which correspond to about 1 amp/cm^2. As salt precipitates, the current is restricted to areas still free, and the current density at these places rises until it exceeds the critical current for passivity. In any case, with a suitable electrode and electrolyte, one may expect to draw currents of about 1 amp/cm^2 before the anode is passivated.

The current in the passive region corresponds, as noted above, to the rate of dissolution of the surface oxide. It is clear that this current gives directly the rate of corrosion of the anode in the passive region. A corrosion current of 10^{-7} amp/cm^2 corresponds to oxidation of 3.2×10^{-5} equiv/cm^2/ year or, assuming a two electron oxidation, e.g., Mg $\longrightarrow$ Mg^{++} + 2e or Fe $\longrightarrow$ Fe^{++} + 2e, and an atomic weight of about 50, to the loss of 8×10^{-4} grams per cm^2 per year. Expressed in another way, the corrosion loss in the

passive state is less than approximately 0.05 mils per year. A five-year shelf life is, therefore, easily achieved with loss of about 0.5 mils of electrode material. If the passive current is 10^{-8} amp/cm^2 (as it is, for example with certain alloys), the battery life for the same loss of material would, of course, be larger by an order of magnitude.

Activation of the electrode can be achieved by reducing the surface oxide by a cathodic pulse. The magnitude of the pulse could be adjusted to cause reduction in, say, less than 0.1 sec. The required current can be estimated as follows: Let it be assumed that the oxide layer is of the order of 30 A thick, as it is, for example, for Fe, Ni, etc. This corresponds to about two layers of oxide with total charge, for reduction, of about 500 μ coul/cm^2. Therefore, the required cathodic current for activation is

$$i_c \ \tau \qquad \sim 5 \times 10^{-4} \quad coul/cm^2$$

and if $\qquad \tau \quad = 0.1 \ sec.$, then

$$i_c \ = 5 \times 10^{-3} \ amp/cm^2$$

It is found in practice that somewhat smaller currents ($\sim 10^{-3}$ amp/cm^2) will cause activation in times of about 0.1 sec. The reduction probably involves a certain amount of self-reduction which occurs when the film becomes partially reduced and the underlying metal is exposed to the solution.

In summary, when in the active state, useful currents of about 1 amp/cm^2 can be drawn through the anode; however, the corrosion current in the active state is also relatively high (10^{-4} to 10^{-3} amp/cm^2). When passive, the anode is inactive, does not corrode appreciably, and can be kept in this condition for extended periods. A passive anode can be activated by a pulse of theorder of 10^{-3} amp/cm^2 in times of about 0.1 sec.

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e) Application Methods

The application of the method of anodic protection to primary reserve cells involves the use of an auxiliary power source for a short time. After battery assembly, the anode may be passivated using an external power source with the cathode as an auxiliary electrode. The power source may be a current supply which delivers a current exceeding the critical current for passivity. After passivation, the low current needed to maintain the anode passive can be provided by electrically connecting the anode and cathode through a current-limiting device using a diode.

For activation, the connection between anode and cathode must be broken and a cathodic pulse of about 1 to 5 ma/cm^2 delivered through the anode. Depending on the circumstances of use of the battery, the current pulse may be delivered from a conventional source of power or from a small, secondary battery. The activating current pulse may be adjusted to yield the desired activation time. This time can probably be varied between 0.01 and 1 sec depending on the magnitude of the current pulse, the size of the battery to be activated, the composition of the anode, and the composition of the electrolyte. If a conventional power source is available, the cathodic pulse can probably be increased to achieve activation times of the order of milliseconds.

A block diagram of the proposed mode of operation is given in Fig. 1. The passivating circuit is a constant current source which is disconnected by a transfer switch after the battery is passive. The same switch can be used to uncouple the plates prior to activation of the battery by a cathodic pulse.
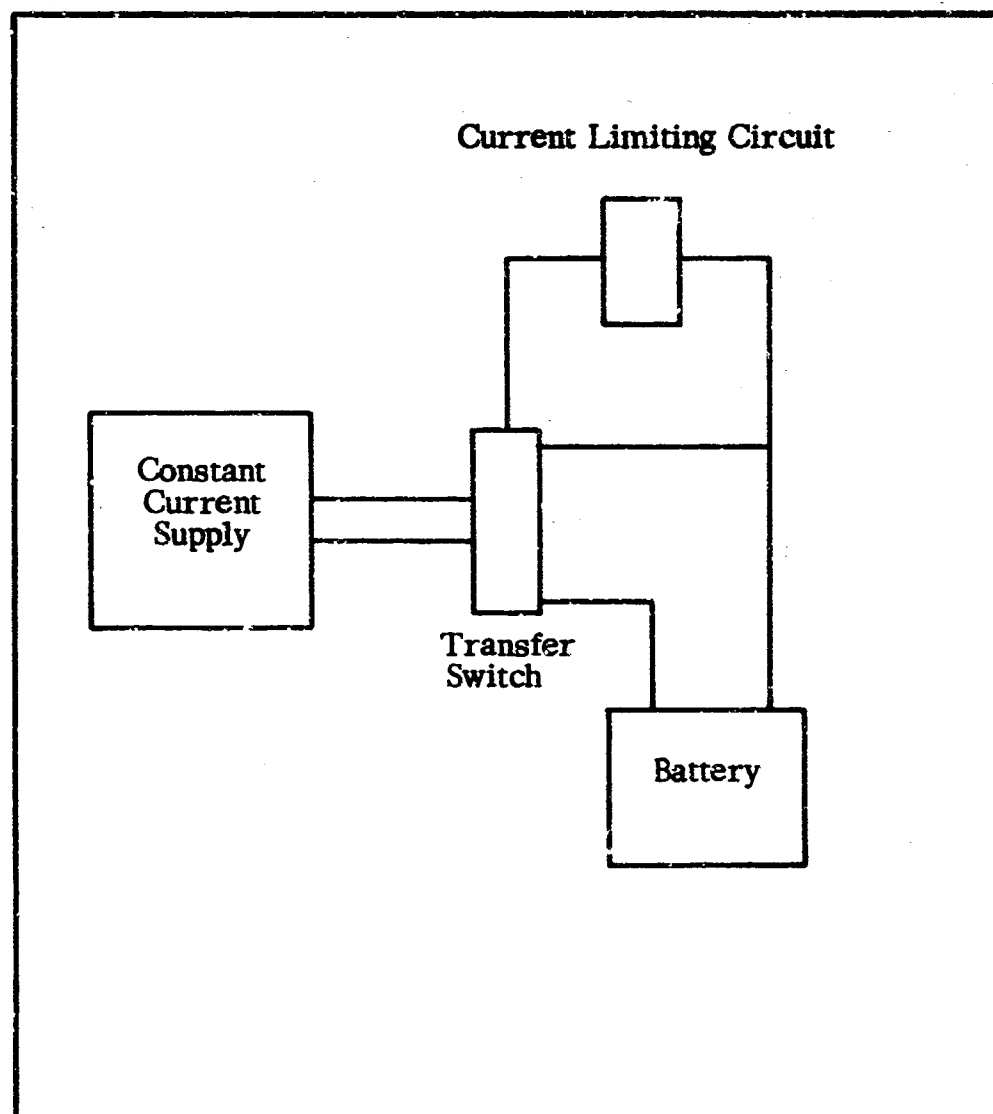
Fig. 1. Block Diagram of Electrical System for Operation
in Passive Mode

II. PREVIOUS WORK ON PASSIVATION OF POSSIBLE BATTERY ANODES

There are a number of reactive metals which are possible battery anodes and which passivate on anodic polarization. From a literature survey of passivation and of battery systems we selected three anode materials for study: iron and alloys of iron, magnesium, and zinc and alloys of zinc. The first system was chosen as a model; the other two were selected because of their application in batteries.

We summarize below the relevant literature on passivation studies of Zn, Fe, Cd, and Mg. References are given in an appendix under "Bibliography." The references on Fe are not meant to be exhaustive but rather illustrative of the phenomena encountered.

a) Zinc: The passivation of zinc has been studied by a number of research groups, most prominently by Huber, by Sanghi, and by Kabanov. The original studies by Huber (Helv. Chim. Acta $\underline{26}$, 1037 (1943); $\underline{27}$, 1443 (1944), were extended by Iofa and co-workers (1949) who studied anodic polarization in Zn in KOH and in KOH containing zincate. They found that the critical current density for passivity increased with increasing concentration of KOH and with decreasing concentration of zincate and that the critical current was temperature dependent. Furthermore, they observed that stirring increased the critical current. These observations suggested that passivation is preceded by precipitation of $Zn(OH)_2$ and that the passive film itself was $ZN(OH)_2$ (of rhombohedral structure).

Sanghi and Wynne-Jones (1958), Sanghi and Fleischmann (1959), and Sanghi and Radhekrishnan (1960) studied the galvanostatic and potentiostatic passivation of Zn in KOH and in zincate solutions over the concentration range of 0.01N to 6N KOH. They found that in the active range the main electrode reaction is the formation of zinc ions; this is followed by a potential range in which $Zn(OH)_2$ precipitates and eventually by the passive range in which a passive film is formed. They also observed a dependence of the critical current on stirring, an observation which has since been confirmed by a number of investigators.

Kabanov and co-workers (1960, 1962) studied passivation of Zn in alkaline solutions and suggested that the passive film is a monolayer of ZnO or of absorbed hydroxyl or oxygen. Using a rotating electrode, they determined from galvanostatic curves the charge associated with the formation of the passive layer. This quantity is proportional to the KOH concentration; it is about 1 millicoulomb/cm^2 in 0.1N KOH, and it increases to about 10 millicoulombs/cm^2 in 0.6N KOH.

The passivation process was studied using transient techniques by Landsberg and co-workers (1957, 1958, 1963) who also determined the charge corresponding to the formation of a passivating film; they found that in normal NaOH this is about 10 millicoulombs/cm^2. Similar studies by Kaesche (1964) in Na_2CO_3 and in $NaHCO_3$ showed that passivation is more readily achieved in carbonate solutions.

The question of the precise nature of the passivating film is not settled. It has been suggested that this film is chemisorbed hydroxyl; alternatively, that it is $Zn(OH)_2$; or again that it is ZnO. X-ray studies by Inoue and co-workers (1954) have identified in the passive state surface films of α-ZnO $\cdot$ H_2O and ZnO. However, these studies were carried out with relatively thick films. Electron diffraction studies by Yuldasheva and Faizullin (1959) did not detect a definite crystal structure of the passive layer, except after prolonged anodic polarization, when crystalline ZnO films were found. Levin and co-workers (1959) identify the passivating layer as ZnO with a hexagonal lattice.

Studies of the passivation of Zn alloys are very limited. Prazak studied the corrosion and passivation of a 75% Sn - 25% Zn alloy in N NaOH. He suggests that the passive layer formed on this alloy has a composition that differs substantially from the passive layers formed on the pure metals; consequently the alloy has a lower critical current and lower corrosion current in the passive state compared with either Zn or Sn. Anodic polarization of Zn-Cd alloys

in N NaOH was studied by Dezider's era and Bychkova (1964). They found that the number of equivalents for passivation increased with increasing Zn content.

The corrosion and passivation of Zn and Zn alloys in acid solutions were studied by Fujino (1956) and by Wakkad, Shams El Din, and Kotb (1958).

b) Iron: The passivation of iron in both acid and alkaline solutions has been studied extensively, and it is not possible to give a detailed account of all this work here.

Passivation of iron in acid solutions has been examined in a series of experimental and theoretical papers originating from Bonhoeffer's group at the Max Planck Institute in Gottingen. This work was continued after his death by a number of his former students, most notably by Vetter. Most of his studies refer to acid solutions and were concerned with the determination of the nature of the passive film and of its properties in these solutions. The passivation of pure Fe in H_2SO_4 was shown to be preceded by the precipitation of ferrous sulfate which restricted the anodic current to pores in the non-conducting $FeSO_4$ layer until an actual current density of approximately 20 amps/cm^2 was achieved (Franck (1951)). The passive film has a thickness in the range of 50 $\overset{o}{A}$, and it corrodes by a chemical reaction (as distinct from an electrochemical process) with a product of ferric ions in solution (Vetter 1955).

The theory of the potential distribution in passive films in Fe and Fe alloys has been discussed in detail by Vetter who suggested a potential distribution within the passive film corresponding to Fe_3O_4 next to the metal and to Fe_2O_3 next to the solution. The equilibrium properties of thin films of FeO were examined by Weil (1963) who showed that deviations from normal behavior occur even with film thicknesses as high as 50 $\overset{o}{A}$. The studies of Vetter lead to an interpretation of the Flade potential which reconciles the observed critical potential for activation with the thermodynamically expected potentials for the iron/oxide systems.

A series of studies of passivation of Fe and of Fe-Cr and Fe-Cr-Ni alloys were carried out by Kolotyrkin and co-workers (1962, 1963) who concluded that the passivation of these materials is primarily due to a chemisorbed film of oxygen rather than to an oxide as such. The controversy between the chemisorbed theory and the oxide theory of passivity has remained an active one, and it is doubtful that a clear-cut resolution between these alternative hypotheses for passivation in acid solutions will be easily achieved.

Passivation of iron in alkaline solutions has been studied by a number of authors. An extensive study of the iron system in alkaline solutions was published in 1947 (Frumkin, Discussions Faraday Soc., $\underline{1}$, 1947). Further work in alkaline solutions was carried out by Kabanov (1954) on iron in 10N NaOH at 20° and $80^{\circ}C$. The passivation current varied from 20 microamp/cm^2 ($20^{\circ}C$) to 1 milliamp/cm^2 ($80^{\circ}C$). The dissolution processes produce $Fe(OH)_2$, and the passive film is probably γ-Fe_2O_3.

Studies of the passivation of iron in alkaline solutions were carried out by Cohen and co-workers (1963) who used a boric acid/borate buffer with pH of about 8.5. They found that the passivation potential was a function of the ferrous iron concentration in solution and of the pH and suggested that it corresponded to the equilibrium potential for the ferrous/Fe_2O_3 reaction. Contrary to the suggestions of Vetter, they inferred that the potential gradient across the passive film is small and that it is mainly due to a higher defect concentration in the oxide surface and to a lower Fe^{++} concentration at the oxide/solution interface.

The actual thickness of the passive film on iron has been estimated between 15 and 30 $\overset{o}{A}$. Kruger (1963) found by direct measurements with polarized light that a film of about 20 $\overset{o}{A}$ was formed in 0.1N $NaNO_2$. This initial film subsequently dissolved, and a passive film of about 15 $\overset{o}{A}$ was formed. In all cases, even when thick films were present, the thickness of the film responsible for passivity was only 20 to 30 $\overset{o}{A}$ thick.

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c) Cadmium and Magnesium: The behavior of cadmium is in many respects similar to that of zinc: it dissolves anodically by the formation of $Cd(OH)_2$ and it passivates with the formation of an oxide layer of appreciable thickness. The critical current for passivity increases with the KOH concentration and increases with stirring in the same way as for zinc. Ershler and co-workers (1953) found that the passive layer is a small fraction of the oxide formed on anodic polarization and that precipitation of $Cd(OH)_2$ precedes passivation in KOH solutions (KOH concentrations up to 10N). Sanghi and co-workers (1960) found that on passivation, the current is controlled by high-field cation transport through a thick cadmium oxide layer. Shams El Din and co-workers (1961) studied the behavior of cadmium amalgams in 0.1N NaOH. In this case, passivation was caused by the formation of $Cd(OH)_2$ on the surface.

The passivation of magnesium has been studied mostly in connection with treatments designed to decrease its corrosion rate in various atmospheres or solutions. It has been suggested that magnesium is normally either in the passive or trans-passive state in aqueous environments (King, 1963). However, magnesium dissolves actively in acid solutions, for example, in H_2SO_4 solutions. The precise electrochemical behavior of magnesium either in strongly acid or strongly alkaline solutions has not been established, although some studies in 2N KOH have been carried out by Barelko and Kabanov (1953). These authors found that with freshly prepared surfaces, the corrosion rate was of the order of 10 ma/cm^2 but that it decreased to 10^{-8} - 10^{-9} amps/cm^2 for passivated surfaces. It has been suggested that the thickness of the passivating film is of the order of 20 Å and that the loose porous oxide formed on magnesium in these solutions has no appreciable effect on the electrode kinetics.

iii. EXPERIMENTAL

A block diagram of the main experimental apparatus is given in Fig. 2. It consists of a potentiostatic and a galvanostatic circuit, a relay for switching from one to the other, and recorders for potential and current. Details of the instrumentation are given in the figure.

The electrochemical cell is a three-compartment, pyrex cell with a built-in Haber-Luggin capillary. The reference electrode is either a commercial saturated calomel electrode fitted into the cell through an arrangement designed to minimize diffusion of chloride ion into the working compartment or a reversible hydrogen electrode. The counter electrode is platinized platinum and is also separated from the working compartment by a glass frit, so that products of the cathode reaction did not contaminate the working electrode.

The working and counter-electrode compartments were blanketed in "pre-purified" N_2. In the reference compartment we used "tagged" H_2 to fix the potential of the Pt/H_2 reference electrode. Potentials are given against the reversible hydrogen electrode (R. H. E.) in the solution used unless otherwise indicated.

The electrode configuration yielding the most definitive and unambiguous results is that of a solid, non-porous cylinder, disc, or plate. Usually, the working electrode was a polished cylinder ($\sim$1 cm^2 area) which was tapped, threaded, and mounted on a Teflon gasket. Some alloys are too brittle to be threaded, and were, therefore, soldered to a Pt wire sealed through soft glass. The Pt and Pt-alloy contacts were covered with melted Kel-F or with irradiated polyolefin. Experiments were carried out at 30 $\pm$ 0. 2°C in KOH or in other electrolytes as indicated.

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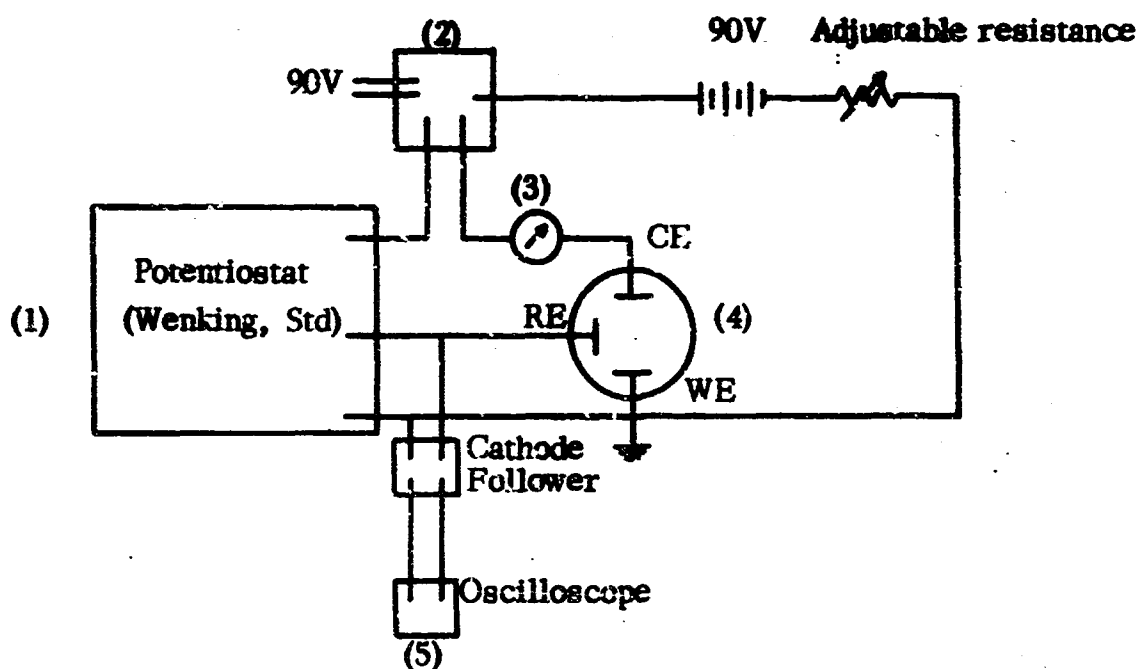
Fig. 2. Block Diagram of Experimental System.

Notes: 1) Wenking standard potentiostat; built-in potential input
calibrated against standard potentiometer; ± 0.1 mv control.

2) Mercury wetted relay, Western Electric Type.

3) Greibach micro-milliameter, 1/2% accuracy.

4) Three-compartment, pyrex cell; S. C. E. or H^+/H_2 as
reference electrode (R. E.); platinized platinum as
counter electrode (C. E.); Haber-Luggin capillary built-in;
the working electrode (W. E.) is mounted in separate
compartment; cell is thermostated $\pm 0.1^{\circ}C$.

5) Oscilloscope or recorder calibrated against standard
potentiometer.

It was decided to do most of the experiments without stirring since these conditions best simulated the conditions in a primary battery. In the case of studies of Zn in KOH, no zincate was added to the solution. The absence of stirring is obvious (dissolution is generally sensitive to stirring), but the absence of zincate perhaps requires some explanation. In a secondary battery employing Zn anodes, the zincate aids recharge and also lessens corrosion on standby. However, neither of these is relevant in a primary battery, particularly a reserve battery.

Where appropriate, the potential was stepped (via an electronic potentiostat) so as to evolve H_2 in between each point. During this treatment any passive films formed previously tend to be reduced. Also, the solution was vigorously stirred for one minute to carry previously dissolved products into the bulk of the solution. The stirring was discontinued for one minute to allow the solution to become quiescent and then the potential of the electrode was raised to the next potential of interest. This procedure was designed to obtain reproducible and appropriate surface and solution conditions. It was not valuable for some materials where passive film reduction was very sluggish.

At the potential of interest, we recorded the current as a function of time and observed any changes in the appearance of the electrode. When the current was steady (after ~60 seconds over most of the potential region of interest, but was generally observed for at least another 5 min), we reverted back to the H_2- evolution potential in preparation for the next point. In this way we were able to obtain currents at a fixed potential which reproduced from sample to sample and during the course of an extended experiment, to within 10%.

For long term tests, the potential was kept fixed in the passive region for periods between 16 and 70 hrs.

Electrodes were prepared from the pure metals (see appropriate sections). Alloys were cast from pure metals and their exact compositon determined by chemical analysis. In all cases, the alloys were examined metallographically to insure that they were single-phase.

IV. IRON AND IRON ALLOYS

This system was selected for study as a model for the operation of a primary, reserve battery in the passive mode.

a) Passivation Studies with Iron and Iron Alloys

Initial tests of the experimental set-up were carried out using iron and iron alloys in acid solutions for which data exist in the literature. The results on solid electrodes were also compared with previous measurements carried out at our laboratory. These measurements also illustrate the sensitivity of the passivation characteristics to metal composition.

The potentiostatic curves given in Figs. 3-6 were obtained by increasing the potential from negative values (from the open-circuit, active corrosion potential) to increasingly more positive values. All the runs were carried out in $6N$ $HClO_4$ at $30^{o}C$.

Iron: Iron in acid solutions shows a broad region for the transition from the active to the passive state, but a very narrow passive potential region. The transition region is broad because a precipitated phase (iron salt) forms on the electrode before passivation sets in. For our purposes, this is of little consequence; the narrow passive region is far more troublesome because it implies a very close control of potential in an actual battery system. In the transpassive region, which begins at about 900 mv, iron dissolves again at substantial rates but now in the Fe^{+3} rather than the Fe^{+2} state.

Iron-Chromium: Iron-chromium alloys containing 2, 4, and 5% Cr were prepared from electrolytic iron and electrolytic chromium. Addition of Cr decreases somewhat the critical current for passivation, and at the same time increases substantially the range of potentials over which the electrode is passive. The critical current is, however, large enough to sustain, even at 5% Cr, 300 ma/cm^2. In this respect, the iron-chromium anodes are acceptable and are preferable to iron in having a broader passive range.

The data for Fe and Fe-Cr alloys are tabulated in Table I.

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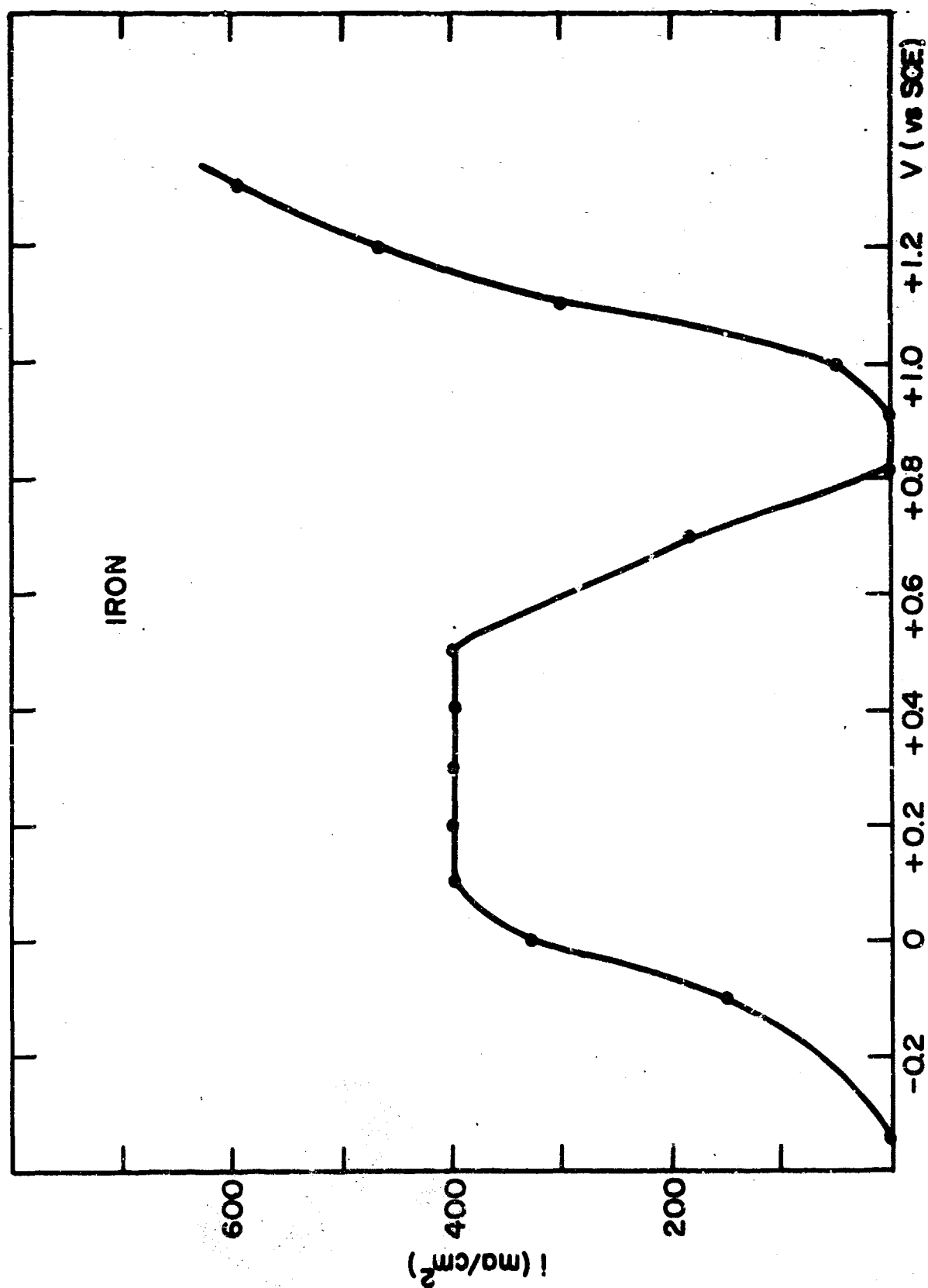
Fig. 3. Anodic Passivation of Iron in 6N HClO$_4$

IRON-2%Cr
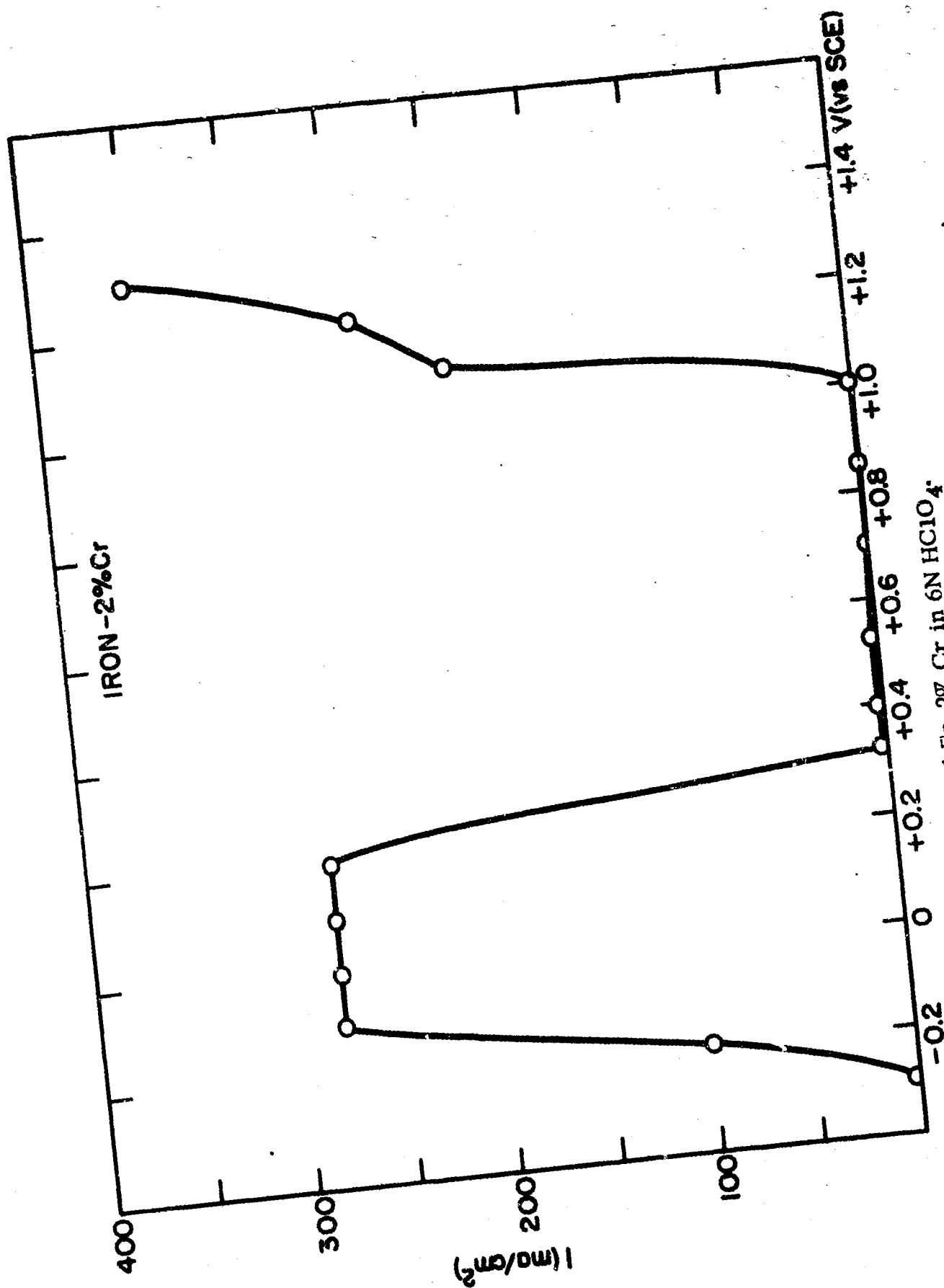
Fig. 4.   Anodic Passivation of Fe-2% Cr in 6N HClO₄.

- 18 -
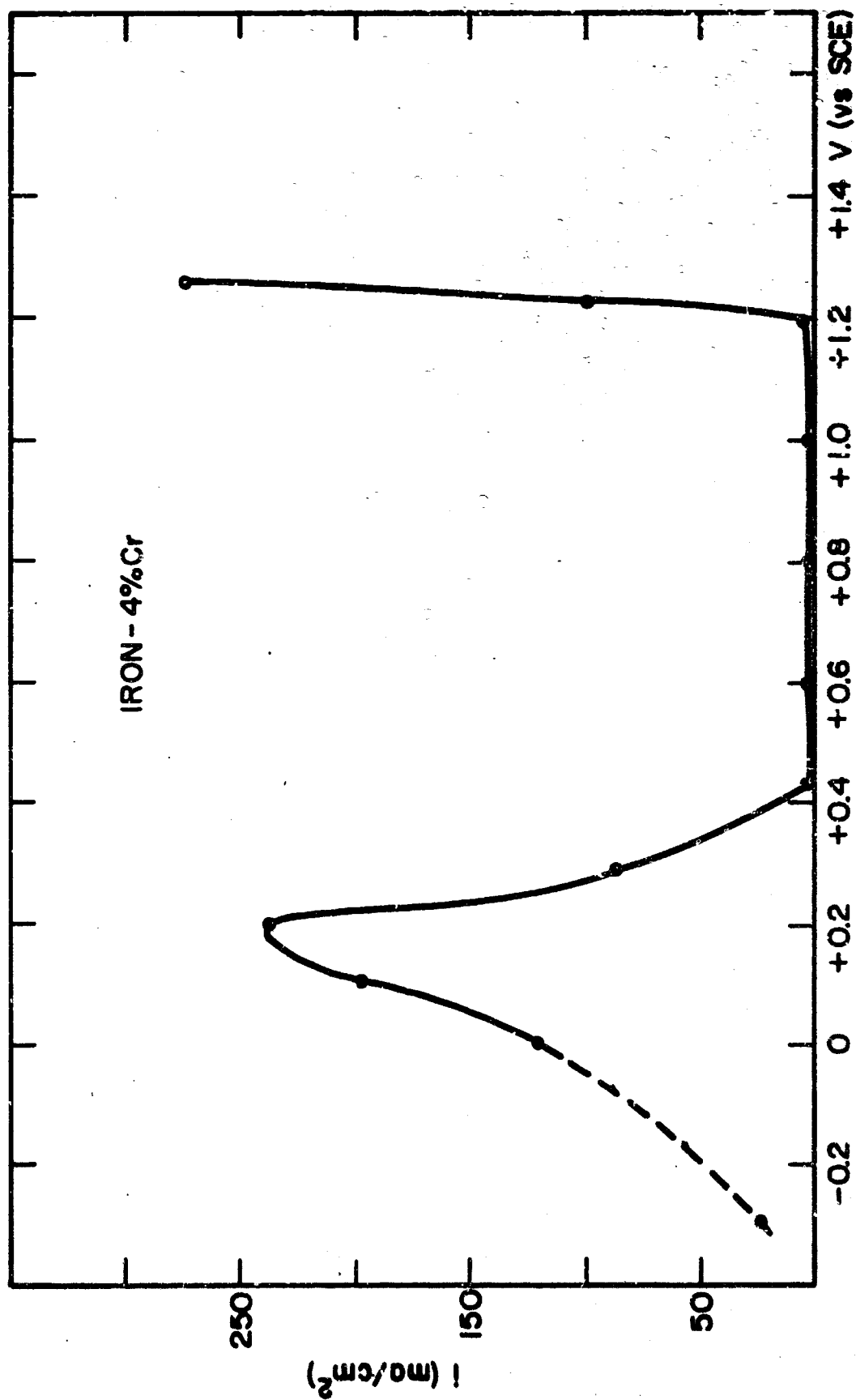
Fig. 5. Anodic Passivation of Fe-4% Cr in 6N HClO₄.

IRON - 5% Cr

i (ma/cm²)

V (vs SCE)
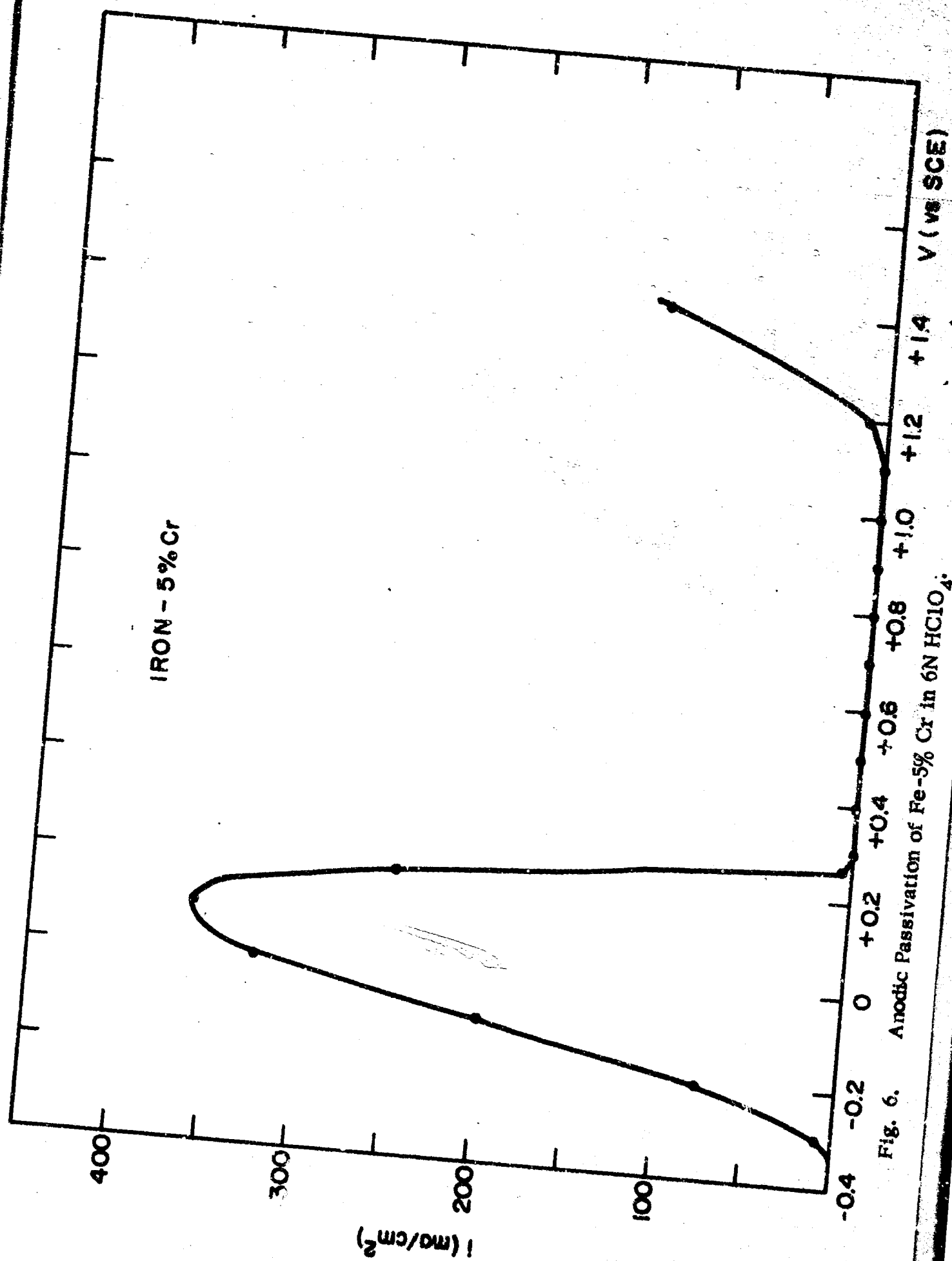
Fig. 6.   Anodic Passivation of Fe-5% Cr in 6N HClO₄.

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Table 1

Passive Characteristics of Iron and Iron-Based Alloys

6N $HClO_4$ at 30°C

All potentials referred to Saturated Calomel Electrode (SCE)

Material	Critical Potential	Critical Current	Passive Potential Region
Iron	-0.1 to 0.5 v	400 ma/cm^2	0.8 to 0.9 v
Iron-2% Cr	-0.1 to +0.2 v	280 ma/cm^2	0.3 to 1.0 v
Iron-4% Cr	+0.2 v	240 ma/cm^2	0.3 to 1.2 v
Iron-5% Cr	+0.1 v	350 ma/cm^2	0.3 to 1.1 v

Galvanostatic Runs

Iron-2% Cr :   Critical current: 250 ma/cm^2

                  Critical potential: - 0.15 v

Iron-4% Cr :   Critical current: 200 ma/cm^2

                  Critical potential: - 0.1 v

Galvanostatic Runs: Galvanostatic runs were carried out with the 2 and 4% Cr alloys (Figs. 7 and 8). The critical current for passivation determined by constant current runs is somewhat smaller than from potentiostatic runs. This is probably due to the fact that a longer time elapses in the active region during the potentiostatic runs and, consequently, the electrode gets rougher. This illustrates the effect of surface roughening when dealing with solid electrodes.

Fig. 7. Galvanostatic, Anodic Passivation of Fe-2% Cr in 6N HclO₄

IRON-2%Cr
GALVANOSTATIC

i (ma/cm²)

300

200

100

-0.4   -0.2   0   +0.2   +0.4   +0.6   +0.8   +1.0   +1.2   +1.4 V (vs SCE)

- 22 -
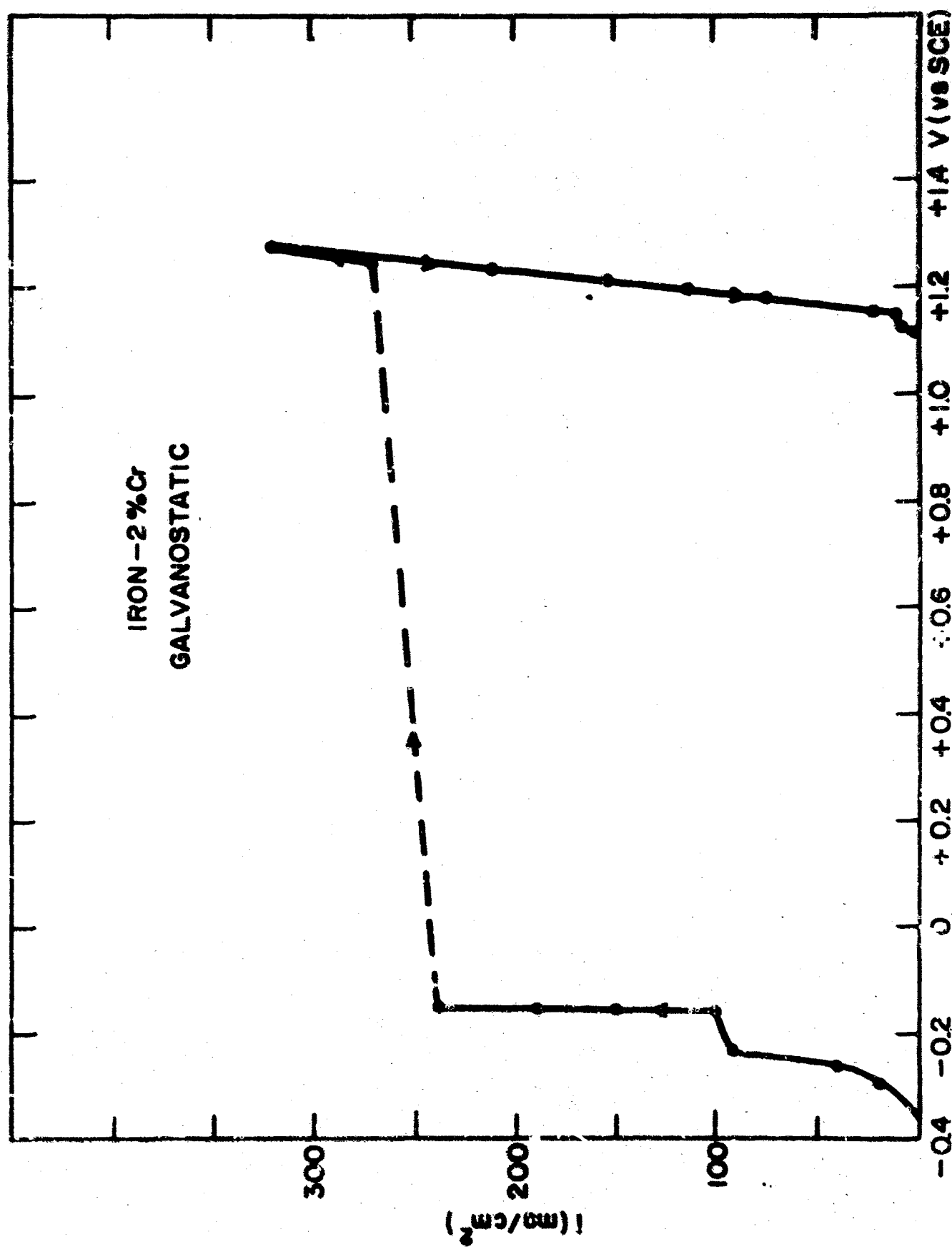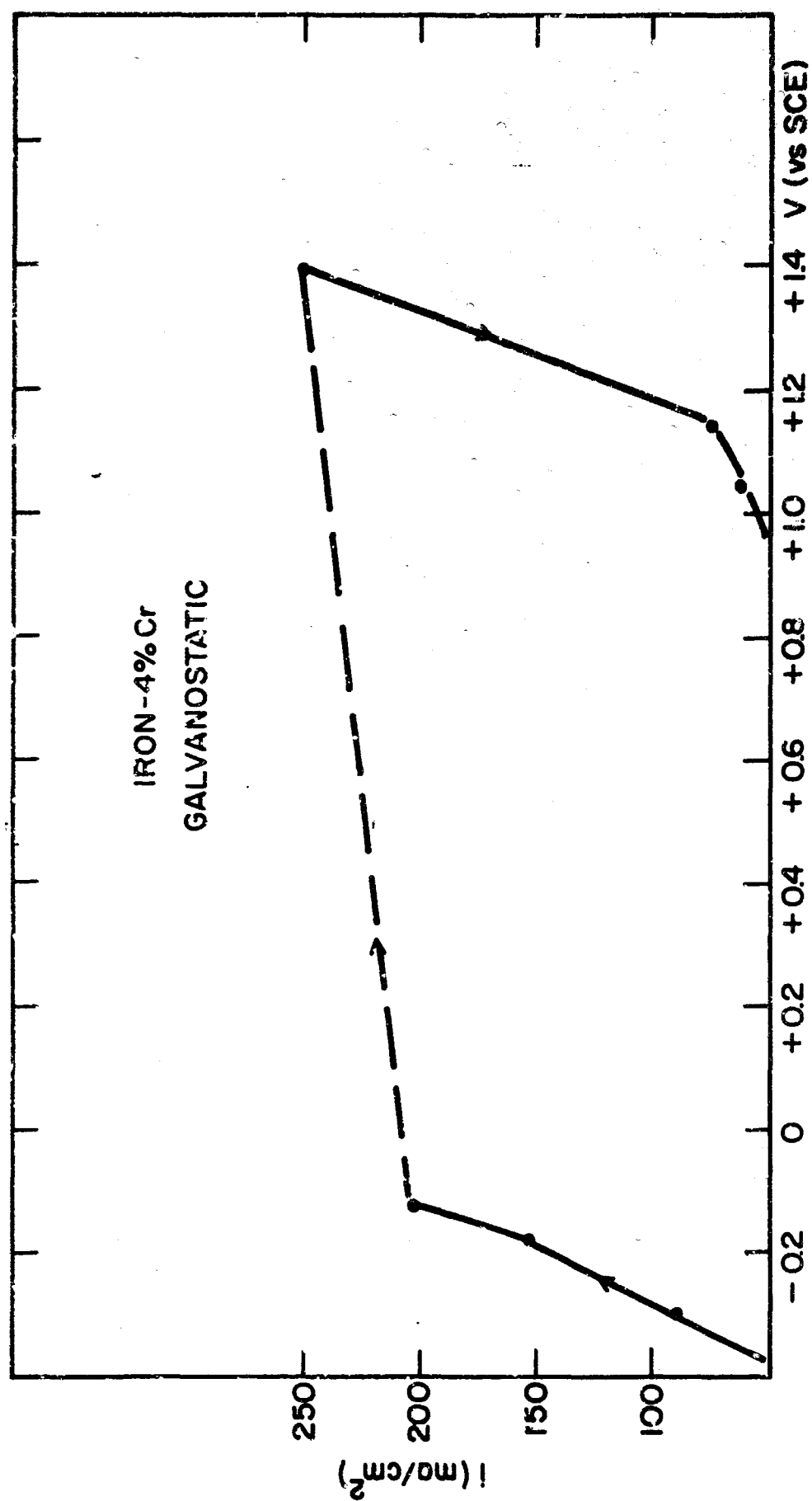
Fig. 8. Galvanostatic, Anodic Passivation of Fe-4% Cr in 6N HClO$_4$

b) Cells Utilizing the $Fe/HClO_4/PbO_2$ Couple

Iron or iron-alloy anodes can be used in acid solution in conjunction with cathodes stable in such electrolytes. The $Fe/HClO_4/PbO_2$ system was selected for study as a primary, reserve battery operated in the passive mode.

Cells utilizing the $Fe/HClO_4/PbO_2$ couple were constructed using PbO_2 electrodes plated on Ni from $Pb(NO_3)_2$ solutions. Electrodes of 25 cm^2 in area were prepared, and a total quantity equivalent to 750 coul of PbO_2 was plated (to yield 30 $coul/cm^2$).

The theoretical energy density of a cell utilizing this couple and operating at 150 ma/cm^2 will depend on the voltage generated at this current density. The practical energy density of such a reserve battery will also depend on its size. For comparative purposes we will choose a battery of 10 v nominal voltage, which will be discharged at 2.5 amps for 5 minutes.

The theoretical weights of Fe and PbO_2 required (assuming 100% discharge efficiency) are:

$$(2.5 \times 300)/10^5 = 0.0075 \text{ equiv (or 750 coul)}$$

wt of Fe: $(0.0075)(28) = 0.21$ g per cell

wt of PbO_2: $(0.0075)(120) - 0.90$ g per cell

At a discharge voltage of 1.5 v per cell, we require 7 cells for a battery voltage of 10 v. We assume an electrode separation of 1 mm (or 40 mils). For a total current of 2.5 amps, we require 2.5/0.15 = 20 cm^2 of electrode area per cell. The electrolyte weight per cell is thus:

wt $HClO_4$: $(20)(0.1)(1.35 \text{ g/cc}) = 2.70$ g / cell of $HClO_4$

where 1.35 g/cc is the density of 6N $HClO_4$. For the total battery we have a theoretical weight of 7 x 2.70 = 19.0 g of electrolyte.

From the above we calculate a theoretical weight of

$$7 (0.21 + 0.90) + 19.0 = 26.8 \text{ g}$$

for active material and electrolyte. For the construction proposed we assume that the weight of container and structural materials will equal that of the active materials and of electrolyte; i.e., total weight is $2 \times (26.8) = 54$ g. The energy density of such a battery is, therefore about

$$\frac{(2.5)\,(10)\,(454)}{(12)\quad(54)} \quad = \quad 17.5 \text{ watts hrs/lb}$$

This estimate includes a realistic allowance for structural components and a somewhat high estimate of electrolyte weight. The major component of weight in the active materials is the weight of the electrolyte, which depends linearly on the electrode separation. We assumed here an electrode separation of 40 mils; this can probably be decreased to 10 mils without difficulty.

Experimental Evaluation of $Fe/HClO_4/PbO_2$ Cell: Cells were constructed using iron electrodes and PbO_2 electrodes plated on a nickel substrate. Each electrode was discharged separately in the electrolyte, and also the complete battery was discharged at a fixed current (by driving the cell at 2.5 amps). The electrodes had an area of 25 cm^2 so that the current density (per geometric unit area) was 100 ma/cm^2. The results are given in Figs. 9-11.

Fig. 9 shows individual potential-time curves for the PbO_2 and Fe electrodes. (In each case a platinum counter electrode was used). Fig. 10 shows discharge of a complete cell without a separator, while Fig. 11 shows the discharge characteristics of a cell with a fiberglas separator. Faradaic efficiencies of about 90% can be achieved at 100 ma/cm^2; the discharge voltage is 1.52 v as against a theoretical voltage for the couple of about 2.1 v (between 2.0 and 2.36 depending on the concentration of Pb^{++} and Fe^{++} in solution). The design characteristics assumed in the above analysis are, therefore, met in general.

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c). Difficulties of a Passive, $Fe/HClO_4/PbO_2$ Primary
Reserve Battery

There are a number of difficulties presented by this couple
when operated in the passive mode. The main difficulty is the high
corrosion rate and small potential region of the passive state of run
in 6N $HClO_4$. One possible way of overcoming this difficulty is to
use Fe-Cr alloys. The Fe-5% Cr system was studied further in
6N $HClO_4$, and the corrosion rate in the passive region was measured
more accurately. The results are shown in Fig. 12.

The corrosion current is in the range of 30 - 50 $\mu a/cm^2$;
it decays to about 1 $\mu a/cm^2$ over a period of 100 hours. This corrosion
rate is acceptable; it can probably be further decreased by alloying
with somewhat greater ($\sim$10%) amounts of chromium.

A second difficulty with this sytem is presented by corrosion
of the PbO_2 electrode in acid electrolytes. This arises from self-
discharge of the PbO_2 (with oxidation of the substrate) through pores,
cracks, etc., in the deposit. A certain amount of exploratory work
on this was done, and it was established that (a) PbO_2 by itself does
not discharge to any noticeable extent, and (b) coherent, continuous,
pore-free deposits of PbO_2 can be plated from $Pb(NO_3)_2$ solutions
onto nickel-plated iron or iron-chromium alloys. However, there is
still the possibility of corrosion in 6N $HClO_4$ if such cracks develop
during storage.

The Fe/Acid Electrolyte / PbO_2 system can be operated
in the passive, reserve mode. Probably, the best conditions for
this couple are 5 ma/cm^2 and 150 ma/cm^2 utilizing iron alloy
anodes, for example, an Fe-5% Cr anode; an electroplated PbO_2
cathode; and an electrolyte which contains H_2SO_4, for example, a
mixture of $HClO_4$ and H_2SO_4.
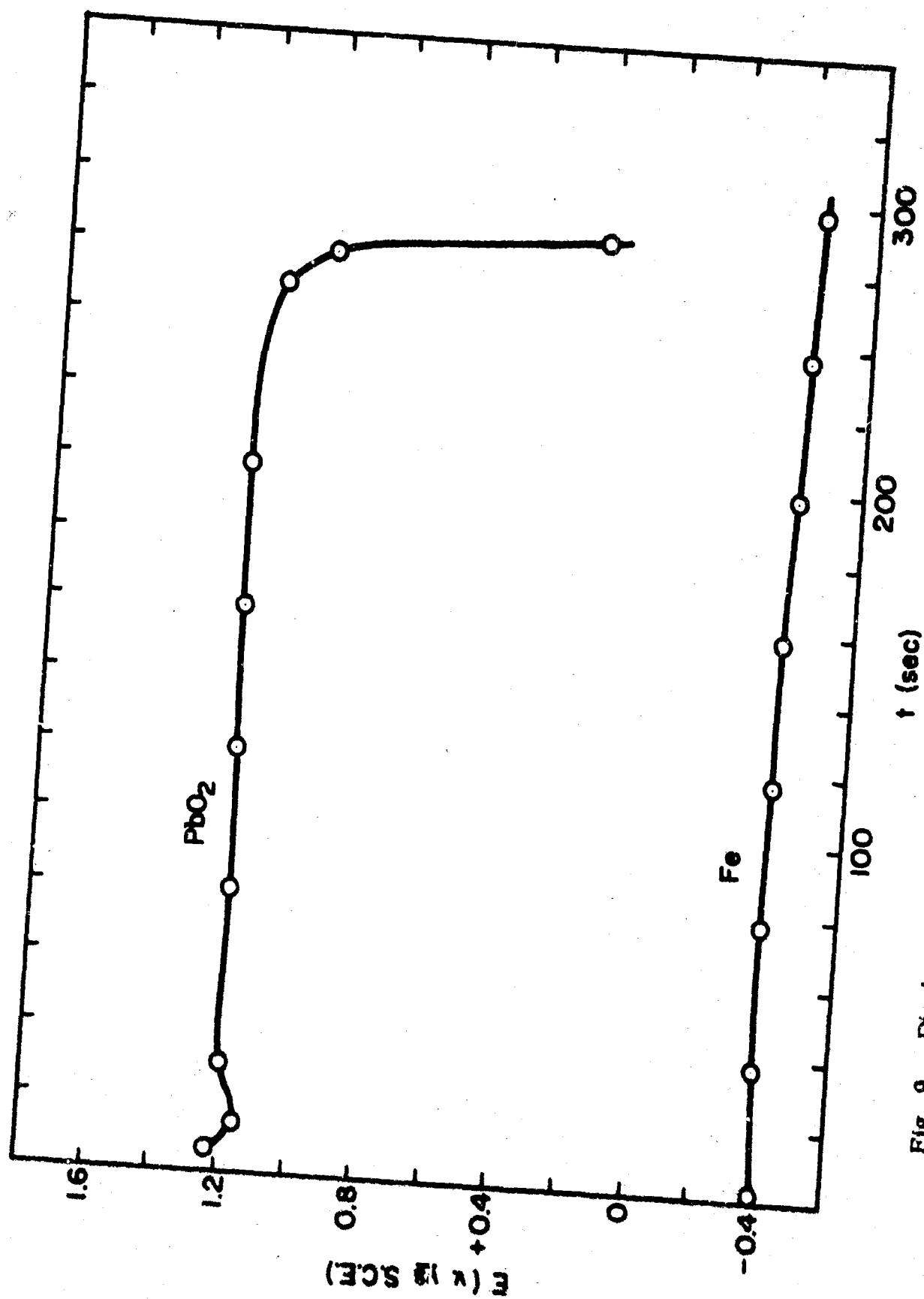
Fig. 9. Discharge Curves for Fe and PbO_2 Electrodes in 6N $HClO_4$
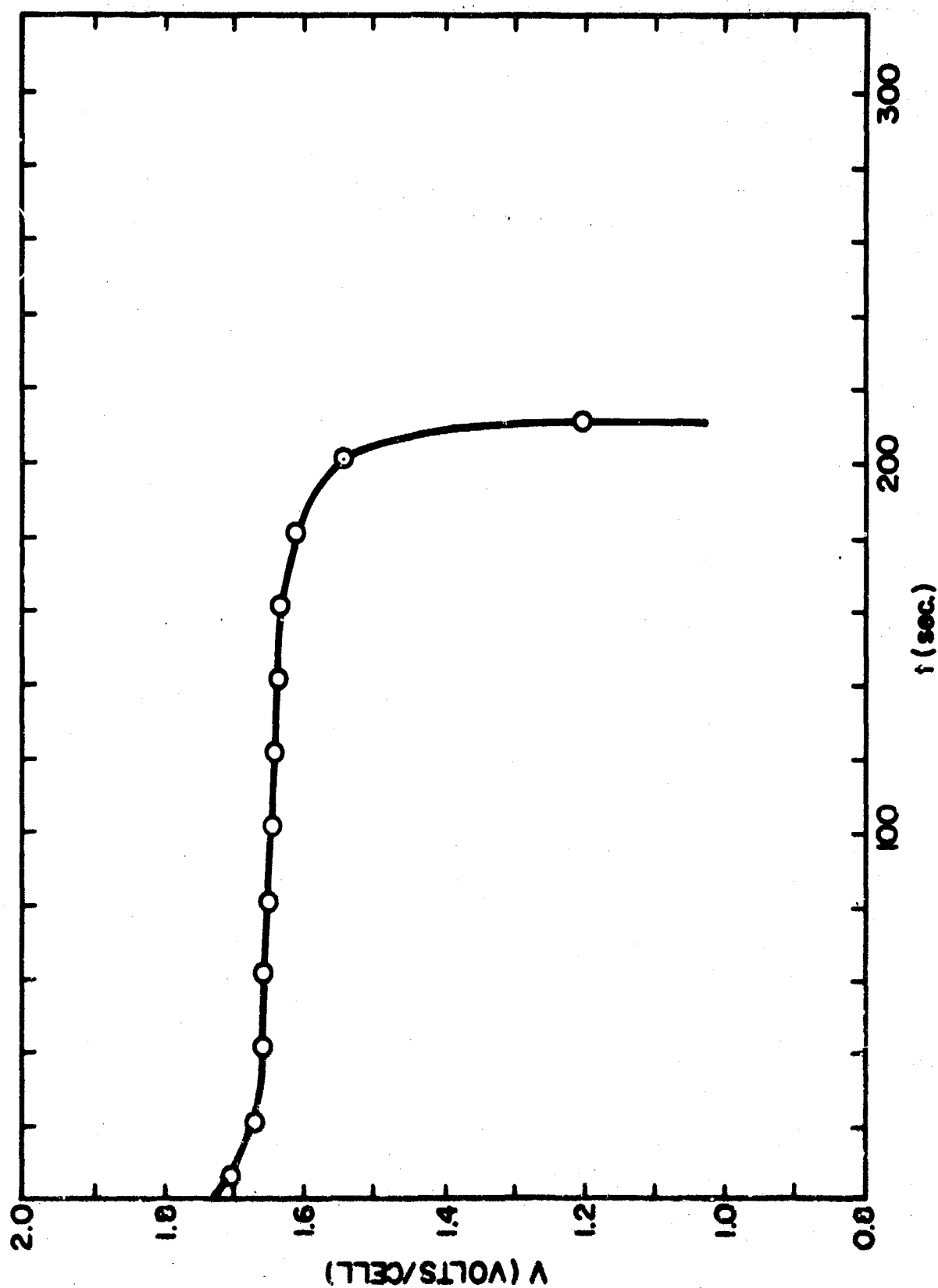
- 27 -

Fig. 10.   Discharge Curve for Fe/HClO$_4$/ PbO$_2$ Cell at 30°C and 2.5 amp (100 ma/cm^2); no separator
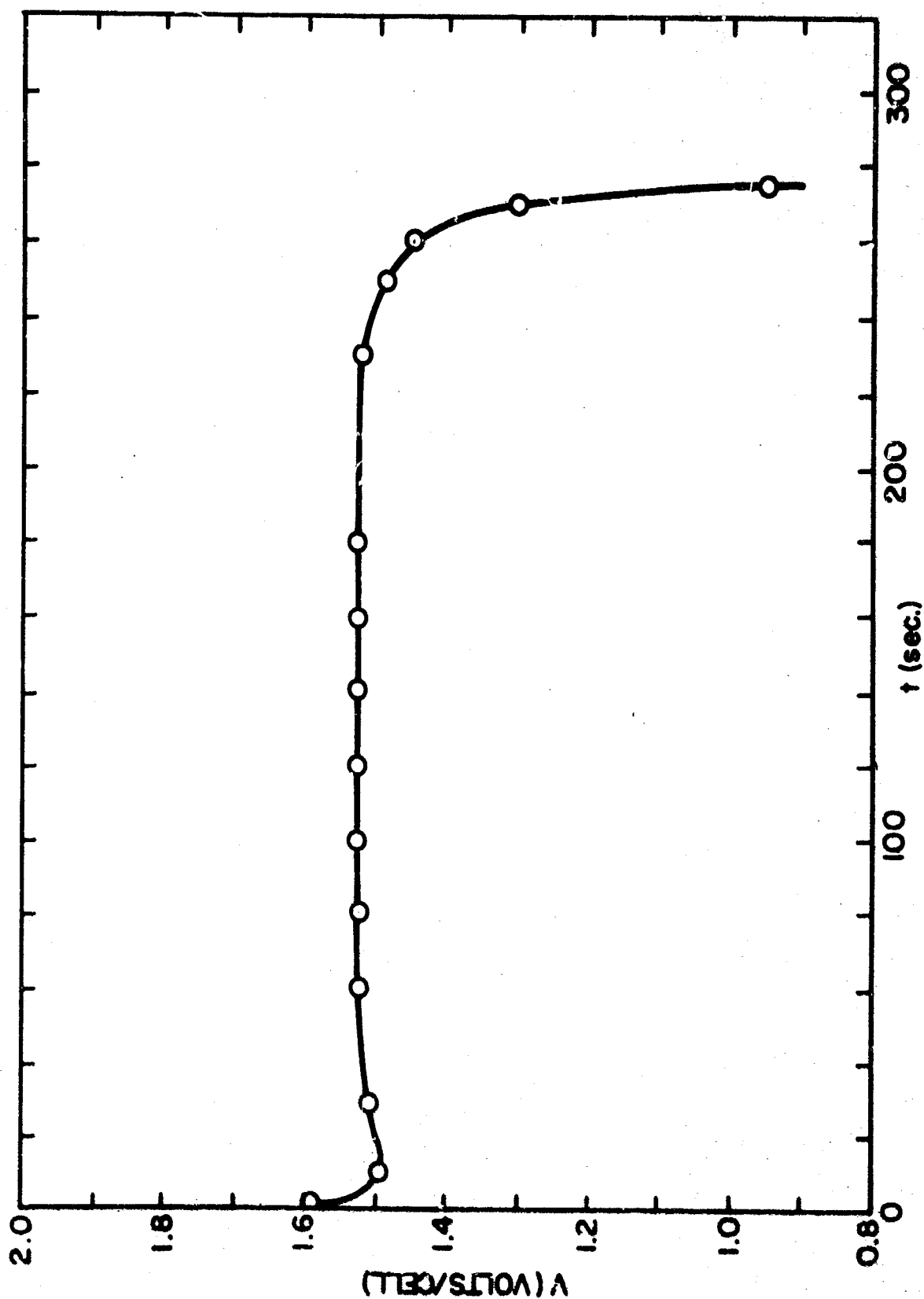
Fig. 11. Discharge Curve for FE/HClO₄/PbO₂ Cell at 30°C and 2.5 amp (100 ma/cm²). fiberglass separator.

- 29 -
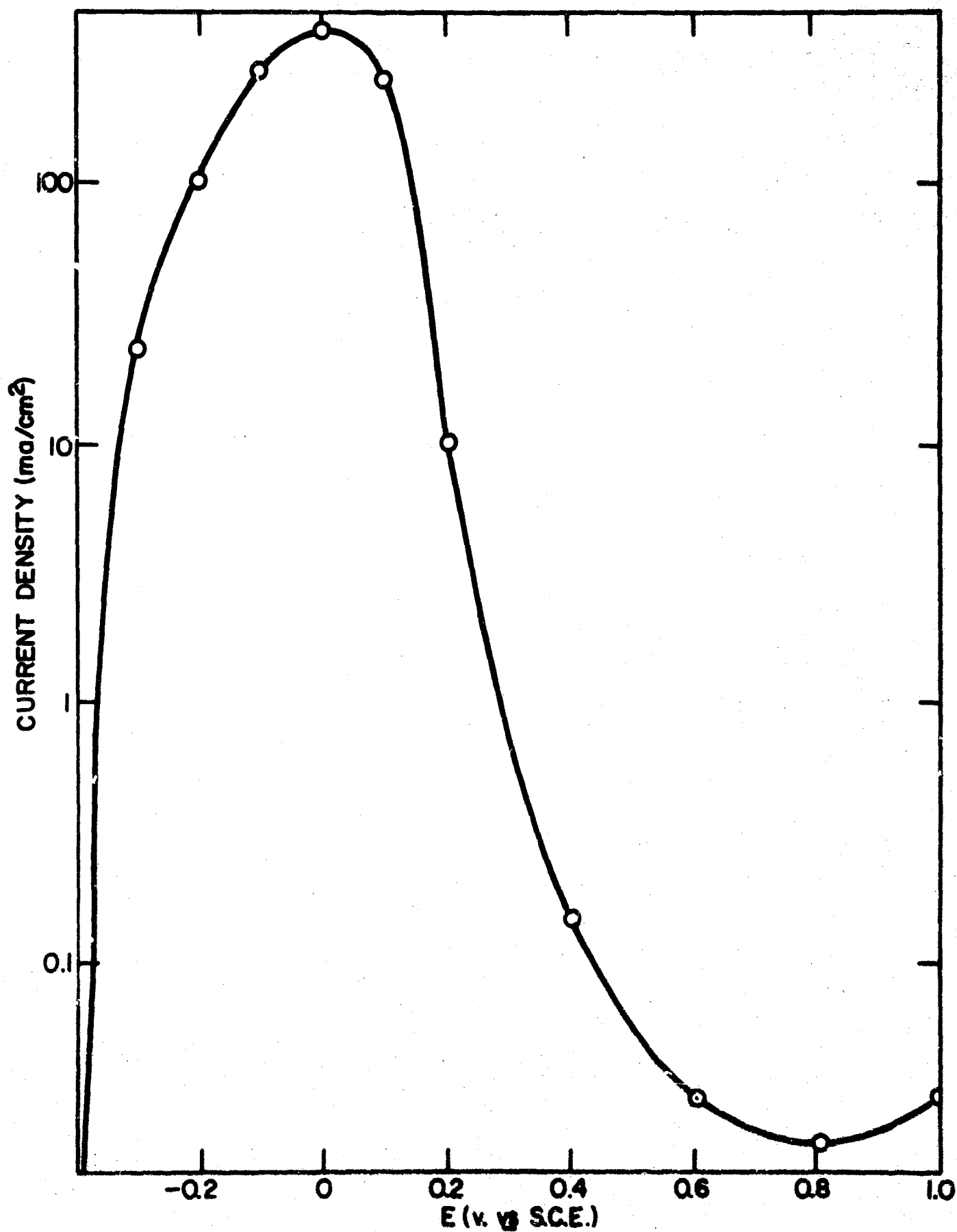
Fig. 12. Potentiostatic, Anodic Polarization Curve for Fe-5% Cr in 6N HClO$_4$

VI. MAGNESIUM AND OTHER POSSIBLE ANODES

a) Magnesium

The Mg anode is of interest because of its theoretical high energy density. In particular, the anode potential is so low that one could couple this anode with the m-dinitrobenzene cathode (the potential of which is only a few tenths of a volt positive to Ht/H_2).

Mg has a very active reversible potential (-2. 4 vs. R. H. E. at pH = C) but, unfortunately, its performance is limited by a high open circuit corrosion rate, by rapid H_2-evolution on discharge, and by rather higher open circuit potentials than one would expect (above - 1. 2v). We have sought to overcome one of the big problems of the Mg anode - its high open circuit corrosion rate, using the passive battery concept.

We have investigated the corrosion of Mg in a number of solutions where it might be used as an anode. In fig. 13 we show the current-potential curves for Mg in these solutions. The results are somewhat approximate at the high current densities because of iR drops. These occur not only in the solution, between the working electrode and the tip of the Luggin capillary, but also in the layer of corrosion products which accumulate on the electrode. This latter makes automatic electronic iR compensation very difficult. The results are presented without correction and the errors are considerable since, for example at + 1. 0 v vs. R. H. E. , H_2 is still being rapidly evolved from the electrode. In all cases, thick white precipitates of corrosion products formed on the electrode. Despite these structures, the curves in Fig. 13 are representative of what would actually be found for a battery anode.

Since the reversible potential of Mg^{+2}/Mg is - 2. 4 v and the open circuit potential is typically -0. 8 v, it is apparent that the open circuit potential is a mixed potential between the H^+/H_2 reaction and the Mg/Mg^{+2} reaction. The major question is whether the intersection of the current-potential curves for these reactions occurs in the active part of the Mg/Mg^{+2} dissolution reaction or where the reaction is impeded by the formation of a passivating oxide. If the latter is true (as suggested by King for neutral and alkaline solutions, J. Electrochem. Soc., 110, 1113 (1963)), the dissolution of a Mg anode must
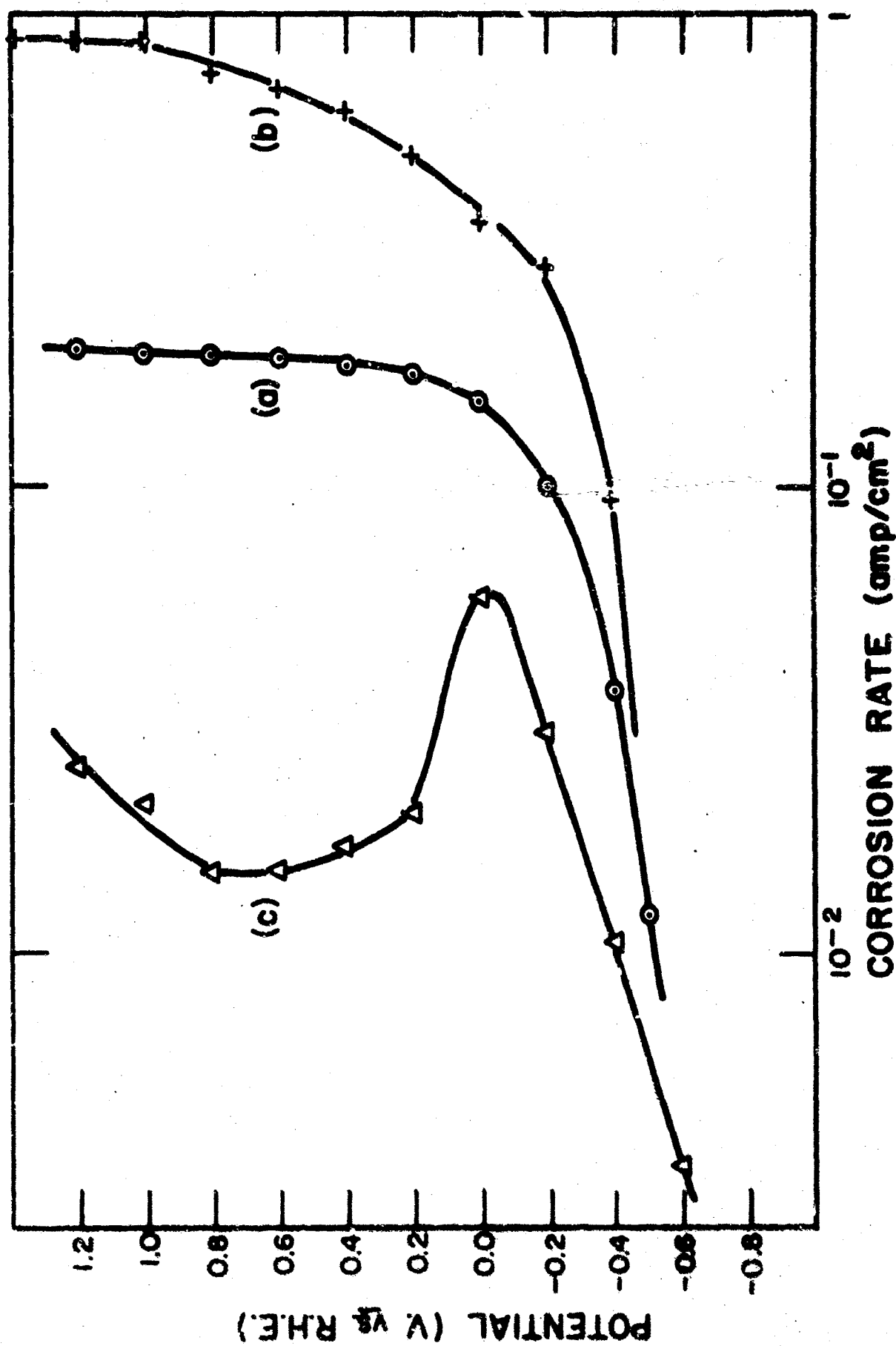
Fig. 13. Anodic dissolution of Mg at 30°C. (a) 1N NaClO$_4$ buffered to pH 7 with NaH$_2$PO$_4$; (b) 1N NaClO$_4$ unbuffered; (c) 0.2M NaF at pH 2 (using HF).

occur transpassively and the passive reserve configuration is not possible. According to Fig. 13 this is the case in pH 7 $NaClO_4$ and pH 7 $NaClO_4$, NaH_2PO_4. In the more acid F^- solution there is some evidence for active-passive transformation but it may reflect the accumulation of macroscopic amounts of MgF_2 which block the surface, rather than the formation of a thin passivating film. Evidence for this was obtained with cathodic galvanostatic pulses from which it appeared that after a few minutes at 1.0 v vs. R. H. E., the ohmic drop was 40Ω and the double layer capacity was only ~ 15 $\mu F/cm^2$ although the electrode was very badly etched.

The behavior of a Mg anode was investigated further in an acid solution (pH = 2.5) of 0.5M Na_2SO_4. We concluded from the polarization curve (fig. 14) that chemical Mg is transpassive in this solution also and therefore unsuitable for our purpose. Addition of $Cr_2O_7^=$, which is reported to improve the corrosion resistance of Mg, did not change the character of the curve (fig. 14).

Another possible way of improving the Mg anode is combining it with a high H_2-overvoltage material, e.g. Hg or Cd. This would lower the open circuit corrosion rate and would tend to eliminate the negative difference effect (H_2-evolution on discharge). Attempt was made to amalgamate the Mg. Acid-pickled Mg was dipped into Hg at $200^{\circ}C$ and the corrosion of the resulting solution of Mg in Hg (up to about 2M in Mg) was examined. It turned out that the Mg in Hg diffuses to the surface of the solution and oxidizes even in air. The amalgam did not form a coherent protective film, as does Mg itself in air, and consequently the amalgam rapidly defoliated, i.e. formed thick layers of a reaction product (MgO, or Mg $(OH)_2$, or, perhaps, Mg_3N_2) on its surface. Rapid H_2-evolution was found even at open circuit in 1M KCl and hence the amalgam was not suitable for our purpose.

b) Other Possible Anodes

We have briefly considered the possibility of using other elements as negative electrodes in an alkaline battery.

Fig. 14 Anodic Dissolution of Mg in 0.5 M Na₂SO₄ of pH 2.5 at 30°C, unstirred.

CORROSION RATE (amp./cm²)

POTENTIAL (V vs. R.H.E.)

0.1M Cr₂O₇⁻²
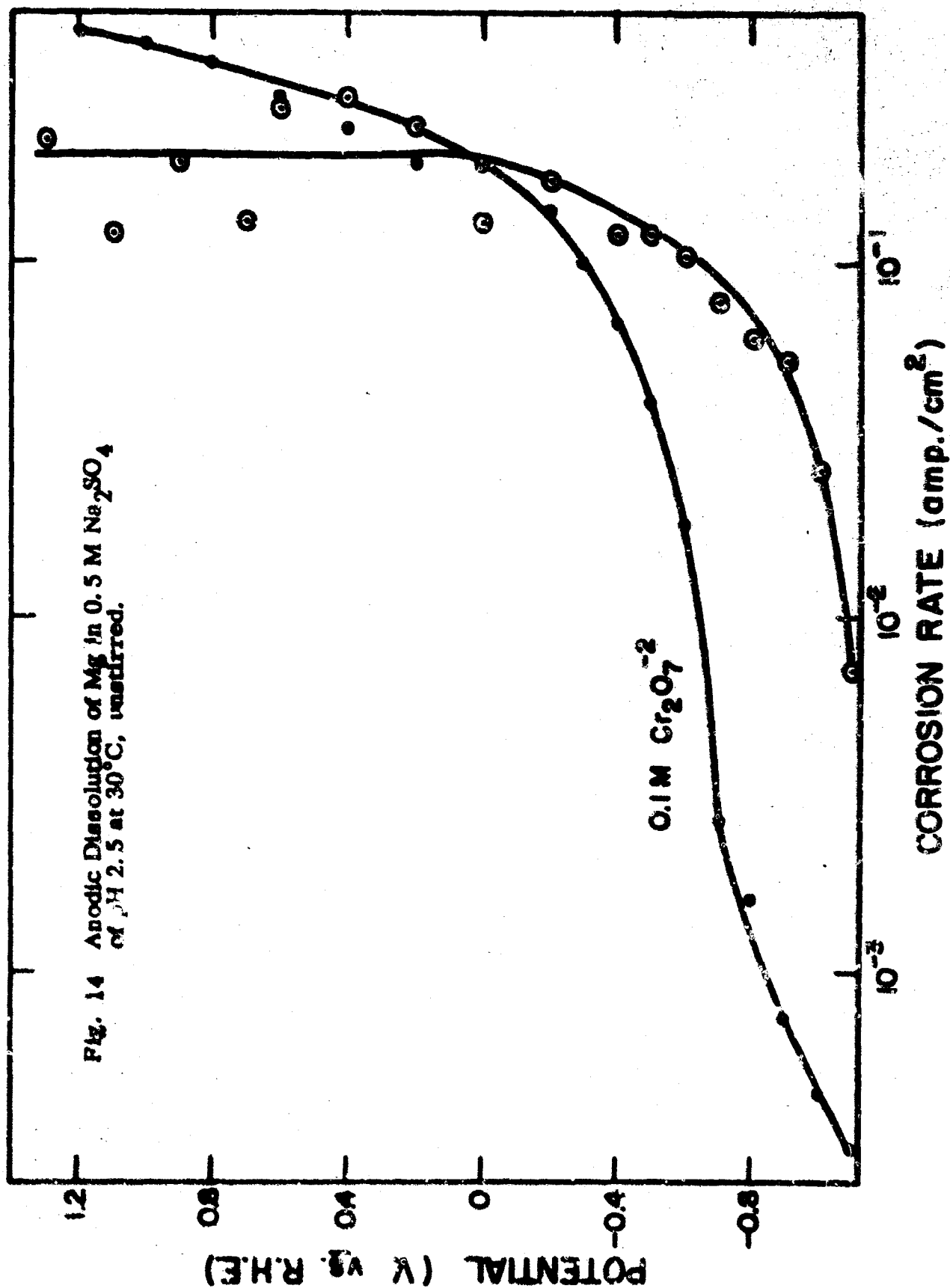
1. Aluminum

Al shows the same phenomena in dilute acid solutions as does Mg. Thus, the open circuit potential is very high: current-potential curves similar to those in Fig. 14 are found, and as with Mg, H_2 evolution increases as the potential increases (the "negative difference effect").

In alkaline solutions (Fig. 15) Al is also apparently transpassive, although the rapid H_2-evolution under discharge is not seen. H_2-evolution at open circuit (-.98 v) is apparently ~ 1 mA/cm^2 (Fig. 16) and, in fact, dissolution is obviously occurring below open circuit so that the evolution is a little higher than shown in Fig. 16. Galvanostatic charging, both anodic and cathodic, showed the presence of films on the surface which could be brought to considerable thickness (several coulombs/cm^2) but which readily dissolved on subsequent potential displacement to 0.0 v. However, the obvious transpassive behavior of Al in alkaline solutions (Fig. 15) rules it out for our purpose.

2. Chromium

Chromium is well known for its passive-active characteristics and could conceivably serve as a battery anode.

Figure 17 shows the dissolution of Cr in 1N and 6N KOH. In both cases the active dissolution of Cr was absent and the open circuit potential was well into the passive region. Dissolution was reasonably rapid above this, but transpassive. Even extended cathodic pretreatment (-0.6 v for 2 hours, where ~ 20 mA/cm^2 of H_2 were evolved) failed to give more than a transitory active dissolution region. Addition of 0.1 M KCl (an excellent passive-film destroyer) to the 6N KOH electrolyte was not successful in revealing an active dissolution region for Cr. We conclude then that Cr is not suitable as an anode material for the alkaline cell.
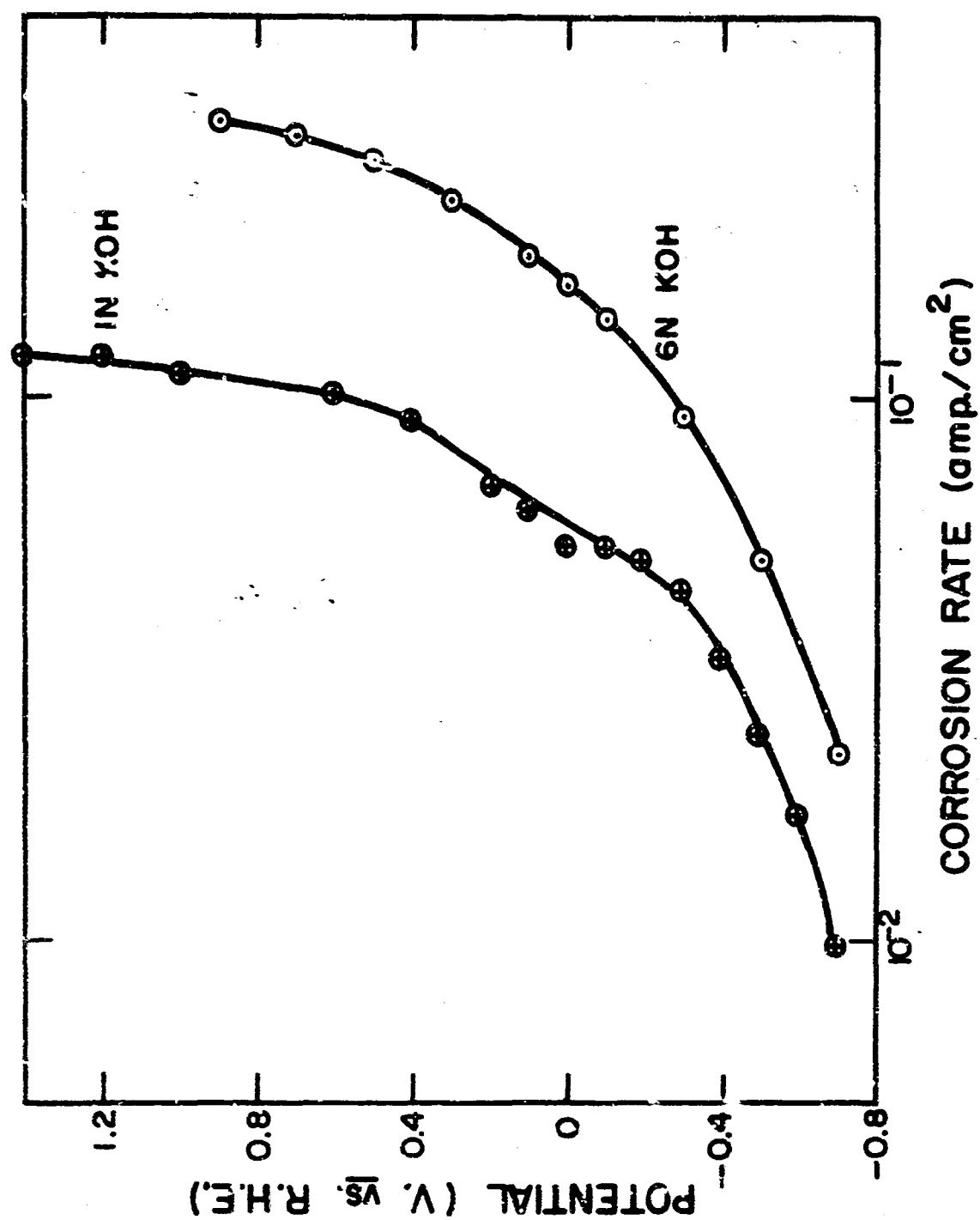
Fig. 15 Anodic Dissolution of Al in KOH at 30°C, unstirred.
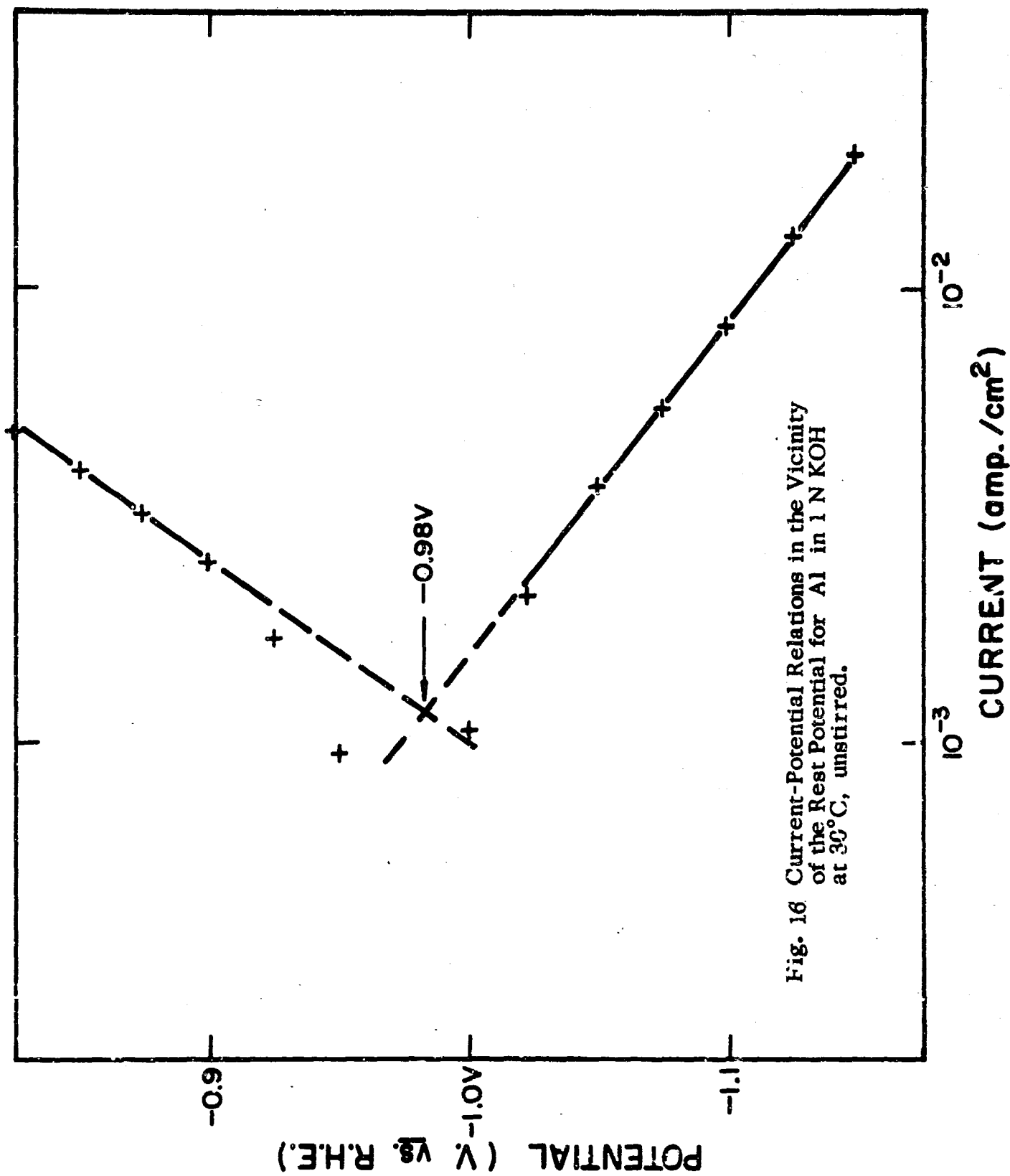
Fig. 16 Current-Potential Relations in the Vicinity
of the Rest Potential for Al in 1 N KOH
at 30°C, unstirred.
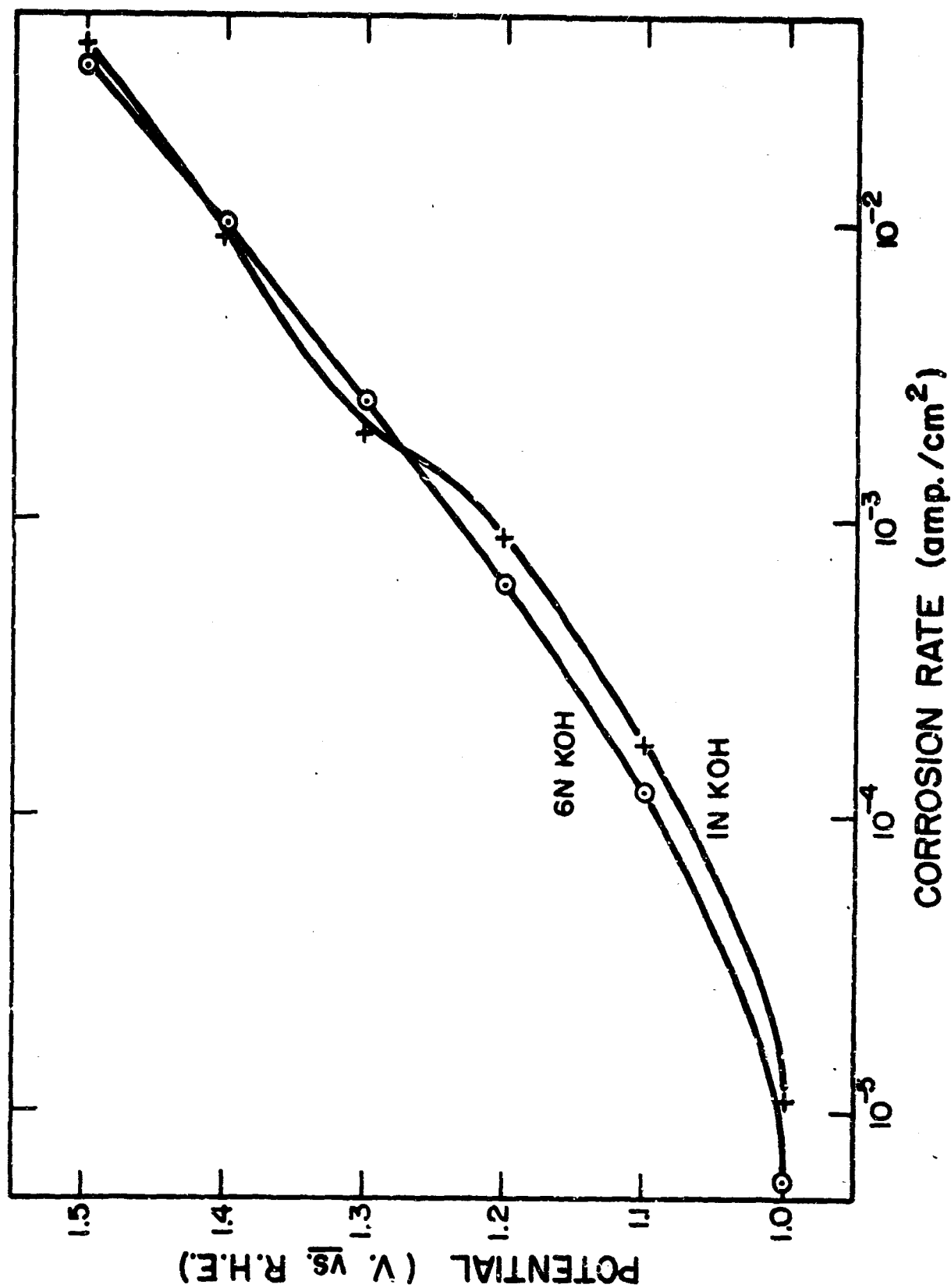
Fig. 17. Anodic Dissolution of Cr in KOH at 30°C, unstirred.

POTENTIAL (V. vs. R.H.E.)

CORROSION RATE (amp./cm^2)

6N KOH

IN KOH

IV. ZINC AND ZINC ALLOYS

Zinc is widely used as an anode in alkaline batteries. Data in the literature suggested that Zn could be passivated in alkaline solutions.

a) Zinc

Typical current-potential curves for Zn is unstirred 1N and 6N KOH at 30°C are shown in Fig. 18. The curves show the characteristic active-passive transition with increasing potential above about -0.1 v vs. R.H.E. The currents were stable with time in the active dissolution region (less than 10% change from 1 - 10 min at each potential) but less so in some parts of the passive region. For example, in 1N KOH, at +0.1 v, $i_{1\ min}$ was 3.9 mA and $i_{7\ min}$ was 3.7 mA. The electrode was white under these conditions (probably $Zn(OH)_2$). Similarly at 0.6 v, where the electrode becomes brown, $i_{1\ min}$ was 6.0 mA, $i_{7\ min}$ was 5.5 mA and $i_{45\ min}$ was 4.5 mA. The largest change with time is seen in the transition region between the active and the passive regions (-0.35 to -0.1 v). For example at -0.1v, $i_{1\ min}$ was 7 mA and $i_{10\ min}$ was 3.7 mA. The variation with time in 6N KOH, where the dissolution rate is much higher, was even less. The colors which the electrode took under the various conditions of polarization are also indicated on the graph.

As indicated, these curves show that Zn in KOH has the characteristic active-passive dissolution curve and the one required for the present purpose. However, while the active dissolution rate is suitably high, the passive dissolution rate is much too high ($\sim$ 4.5 mA/cm^2 in 1N KOH and 55 mA/cm^2 in 6N KOH under the best conditions). An appropriate passive dissolution rate is perhaps one microampere per cm^2. To achieve this, one can alloy the zinc (either as a solid solution or as in an intermetallic compound) with an element which passivates better in KOH but which still dissolves readily at the anode potential of the Zn-AgO battery.

The factors which must be considered in selecting suitable alloying elements are considered in the next section.

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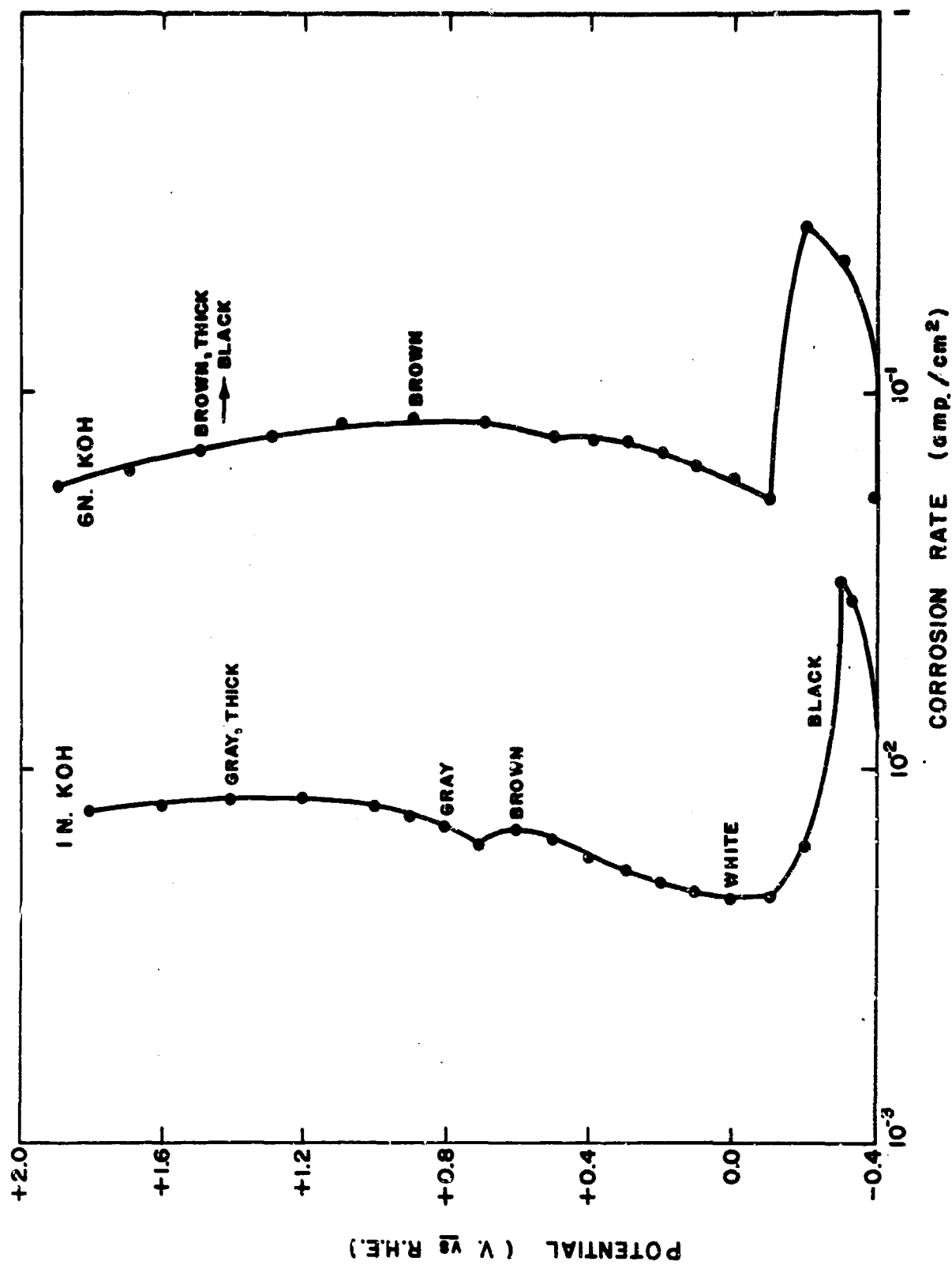
Fig. 18. Anodic Polarization Curves for Zn in KOH, 30°C, unstirred.

b). Factors Governing Selection of Alloying Elements

The factors governing the choice of suitable elements for alloying with Zn have been considered in some detail in this period. One important factor governing the selection must be that the alloying element is as non-noble as possible so that it will not raise the potential of the anode and reduce the power density of the battery. Information about this is readily available (Latimer, Oxidation Potentials (1952) or Pourbaix, Atlas of Electrochemical Equilibria (1963)) although in very alkaline solutions it is of dubious reliability. Another important characteristic of the alloying constituent then must be the ability to form a passive layer in a potential region below the AgO/Ag_2O potential (1.35 v vs. R.H.E.). This passive layer must be readily removable for activating the battery. Accurate information about these aspects, i.e. the actual kinetic behavior of elements in alkaline solutions, is scarce and even less reliable than the theoretical (thermodynamic) information mentioned above. On the basis of thermodynamic considerations and on general electrochemical corrosion grounds, we might attempt to alloy with V, Ti, Zr, Hf, Nb, Ta, Cr, Mn, Fe, Co, Ni, Cu, Cd, In, and Mg. However, alloying Zn with Ti, Zr, Hf, V, Nb, Ta, Cr, and In is either very difficult or impossible. This leaves Mn, Fe, Co, Ni, Cu, Cd, and Mg as reasonable possibilities. Some of these elements are more noble than zinc itself, and this may turn out to be a problem.

Corrosion tests on a number of elements were carried out in KOH to test appropriateness for alloying with Zn.

The current potential curve for Mg in 1N KOH is shown in Fig. 19. This metal approaches the desired passive current but is not readily activated; indeed, we have not really found any significant potential region of active dissolution. (see also Sec. V)

The corrosion of Cu was investigated in 1N and 6N KOH (Figs. 20 and 21). In 1N KOH, Cu shows a typical active-passive transition, being active at 0.8 v vs. R.H.E. and showing a minimum of passive current at 1.1 v. The currents depended very strongly on time. For example, after 45 minutes at 1.0 v, the corrosion rate was $0.6 \mu A/cm^2$ and the electrode was covered with a dull brown film.

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Fig. 19. Anodic Dissolution of Mg in 1N KOH at 30°C, unstirred

Fig. 20. Anodic Dissolution of Cu in 1 N KOH at 30°C, unstirred
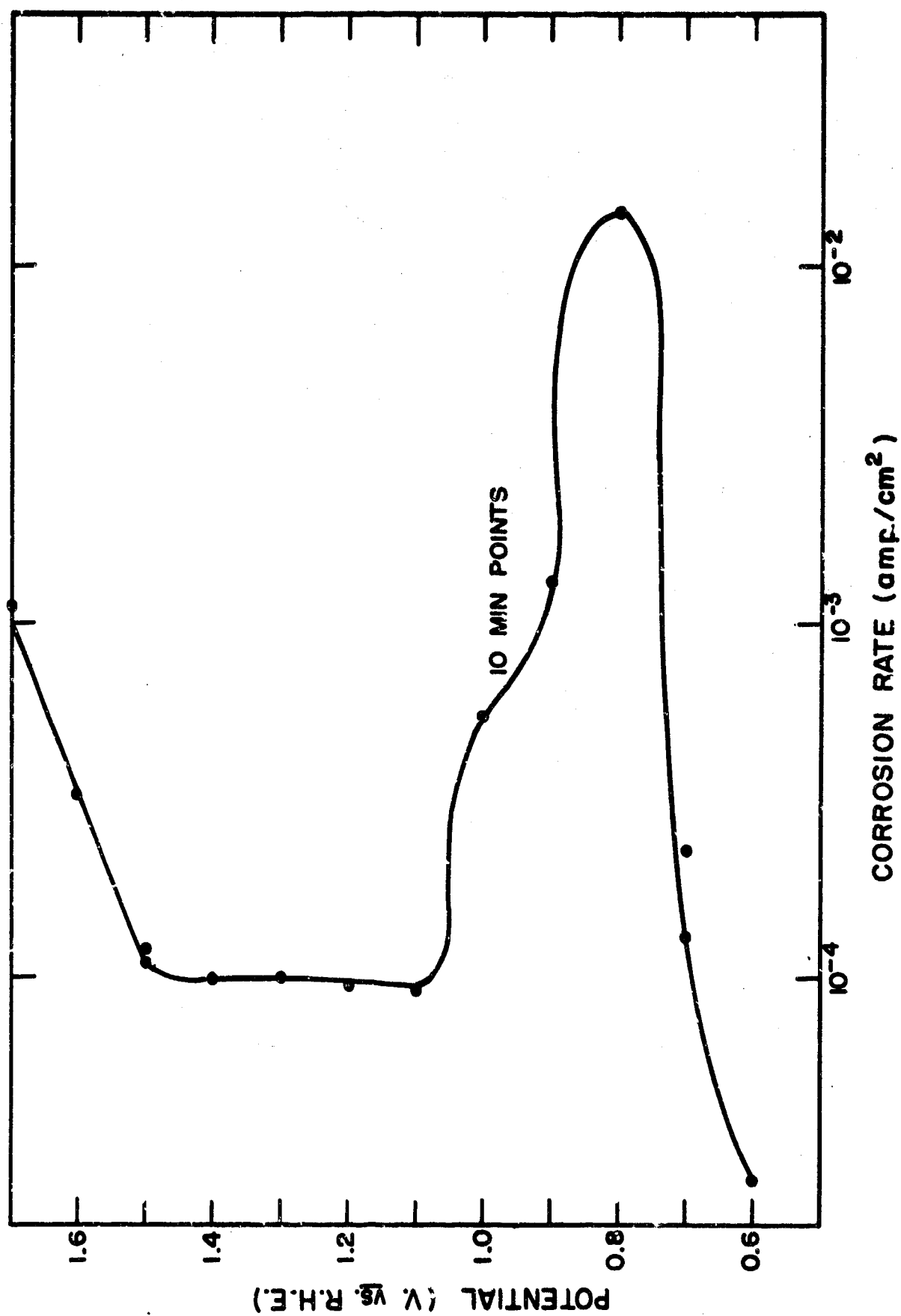
Fig. 21. Anodic Dissolution of Cu in 6N KOH at 30°C, unstirred.

Activation was readily achieved with a cathodic galvanostatic pulse, and a number of potential arrests were seen before H_2 - evolution. The charges involved in these potential arrests were dependent on the current density, suggesting the reduction of solution species rather than (or in addition to) surface oxides. Under some circumstances the electrode acquired black, velvety films which could not be reduced galvanostatically.

In 6N KOH (Fig. 21) the currents were much steadier, but the dissolution rate was considerably higher. For example, the passive current was 10^{-4} amp/cm^2. Again, the electrode went through various color stages in different potential regions. The greater corrosion rate of Cu in 6N KOH is related to complexing of $Cu(OH)_2$ by KOH; for example, we found that Cu $(OH)_2$ is relatively insoluble in 1N KOH and soluble in 6N KOH.

The corrosion of Ti in 1N KOH is of the right order for the present purpose (Fig. 22) although the active dissolution region is so low that activation after standby passivation would be difficult. The passive current is fairly low and, for example, after one hour at 1.0 v falls to about 2.5 μA/cm^2. After being taken to 1.6 v in an extended run, the Ti looks little different from its original condition but reduction of what is certainly a passivating film is very difficult since there are no potential arrests at - 1 mA/cm^2 before H_2 - evolution. In 6N KOH, Ti tarnished after a short while at potentials above the hydrogen potential. Currents were unsteady but low enough to suggest the possible usefulness of Ti in this medium (a few μA/cm^2 after several minutes at 1.0 v). One of the problems with the Ti system is that although compounds with Zn have been reported (Hansen, Constitution of Binary Alloys), they are apparently difficult to make.

The corrosion of Mn in KOH has also been investigated. Corrosion currents were low. (Fig. 23 shows 5 min. points) and rather unsteady, declining rapidly with time. For example, in one experiment at 0.8 v, the current fell from 150 to 50 μA/cm^2 going from 1 to 5 min; at 1.4 v it fell a similar factor in this time range. On reduction from high potentials (e.g. 1.4 v) there was a long potential arrest, suggesting the presence of a
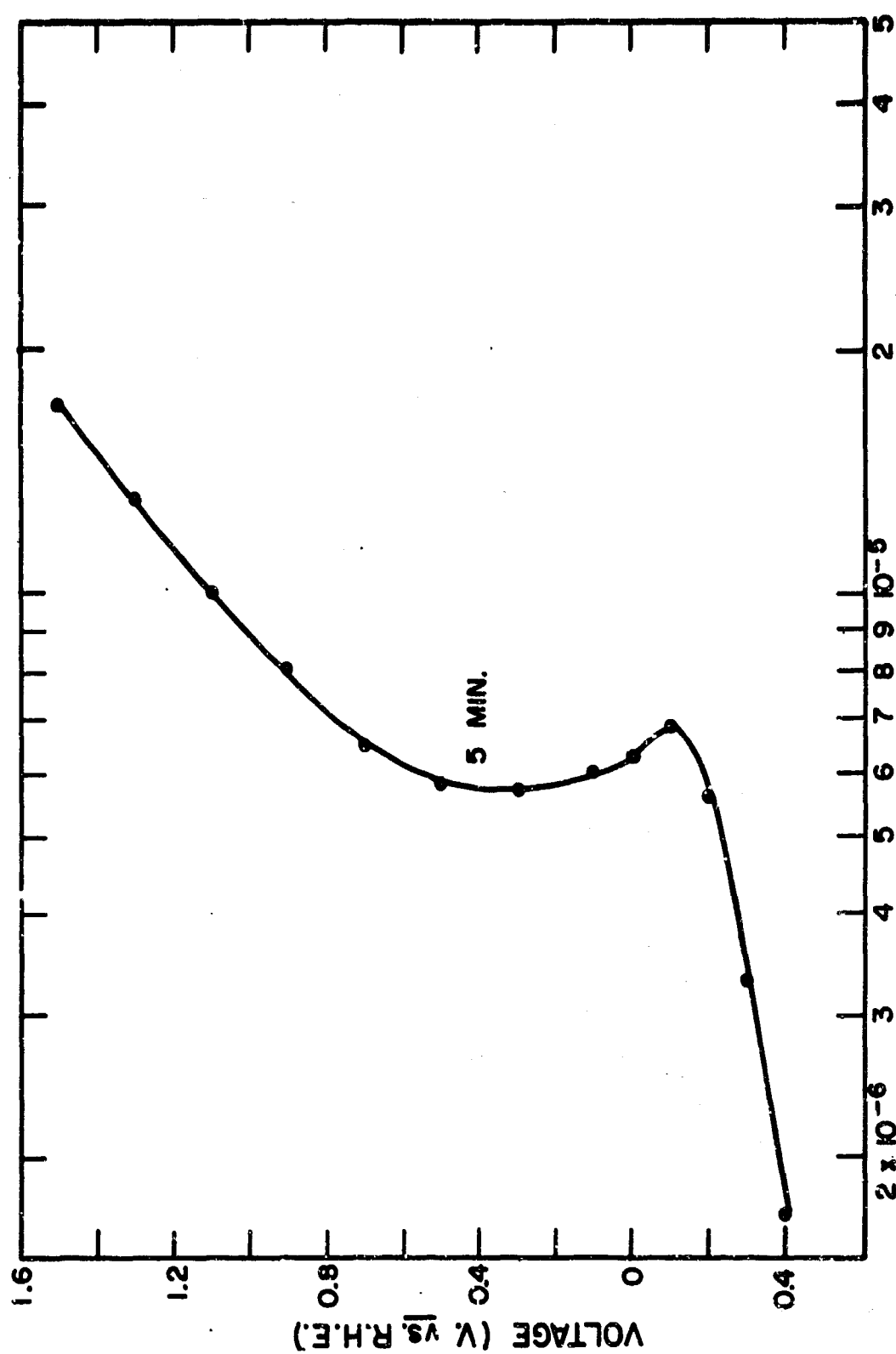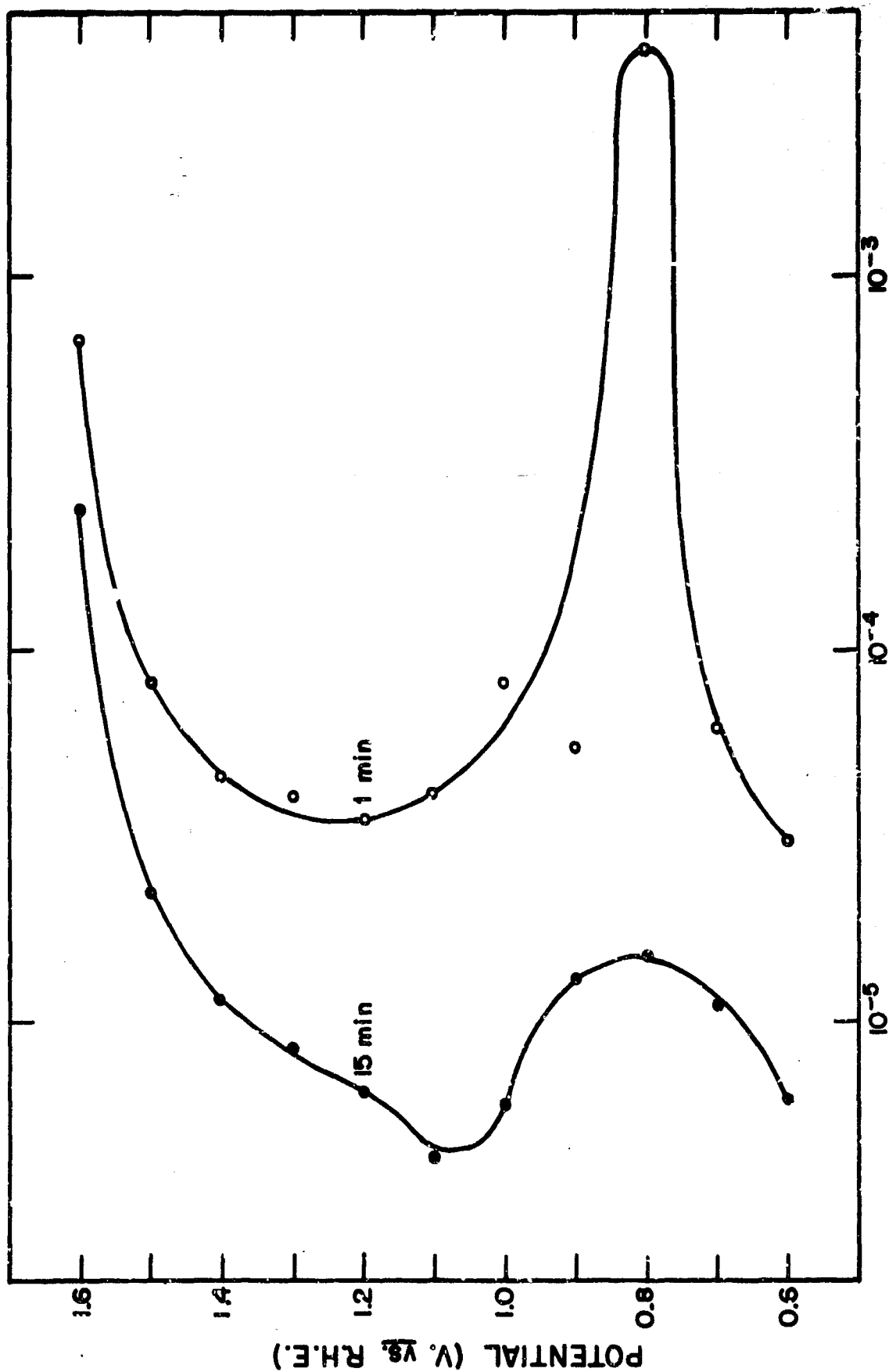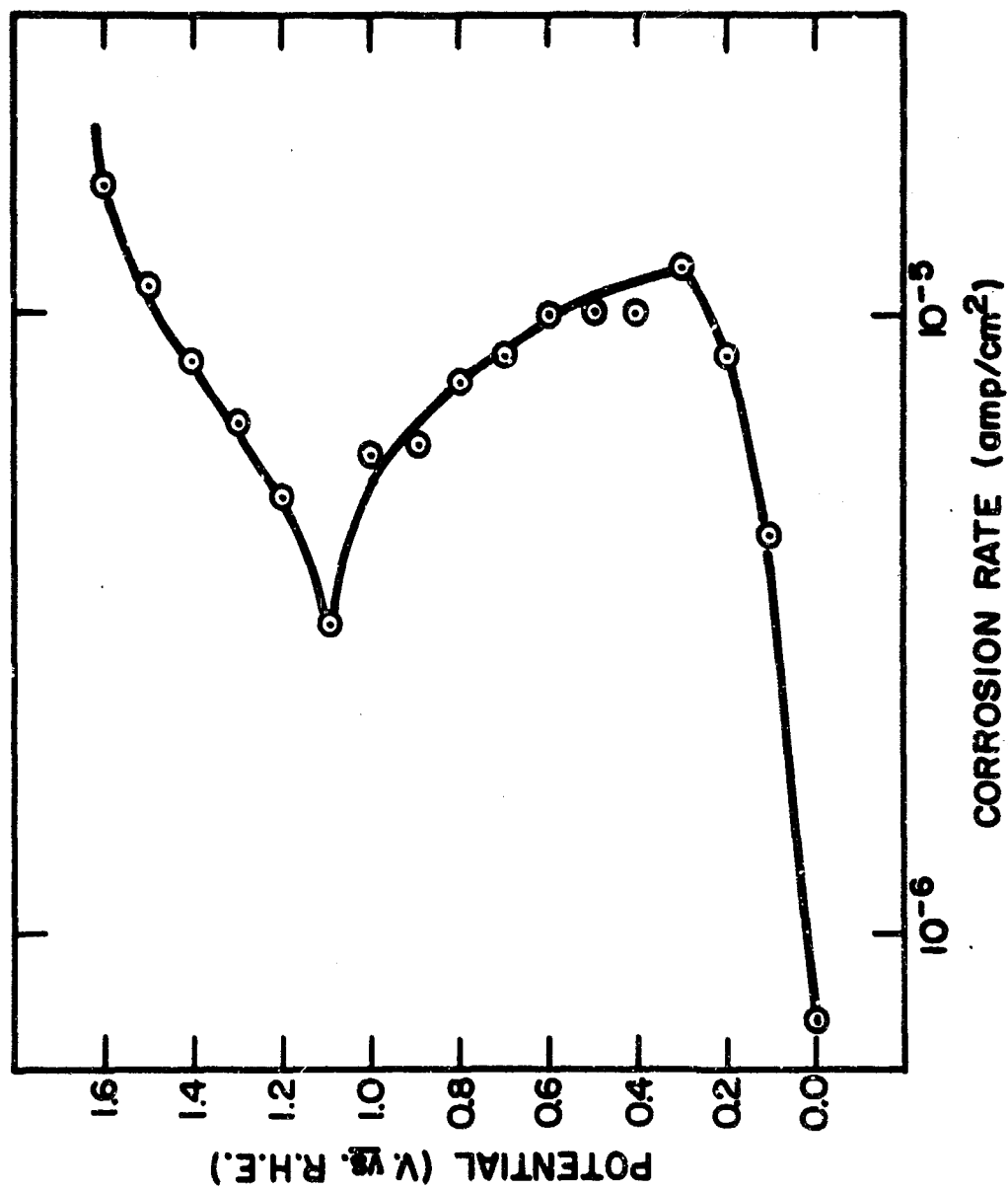
Fig. 22. Anodic dissolution of Ti in 1N KOH at 30°C, unstirred
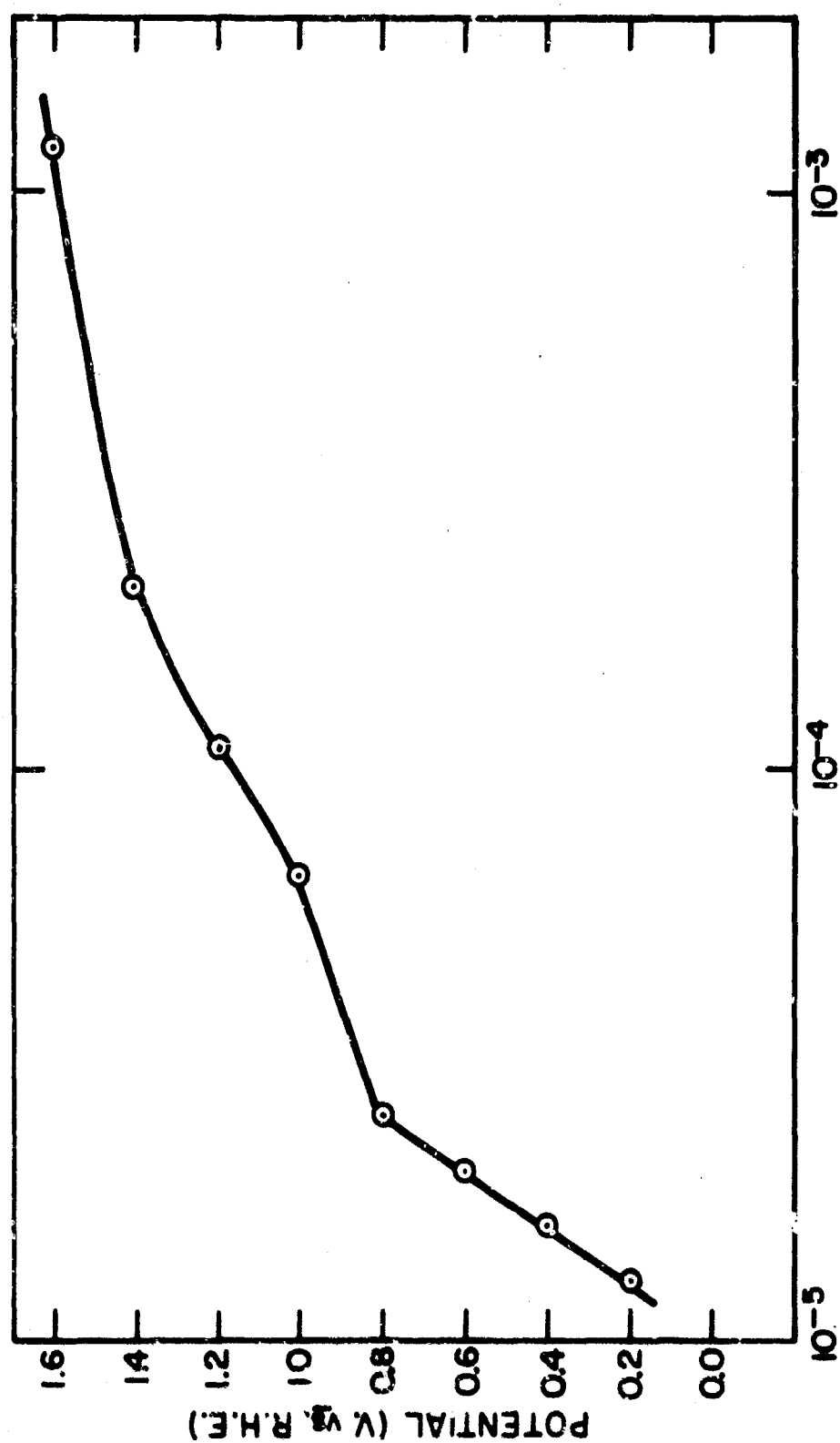
Fig. 23. Anodic dissolution of Mn in IN KOH at 30°C, unstirred

surface oxide. Below 0.6 v, the currents were much steadier but still quite low. The potential of the Mn returns to the H_2-evolution region on cathodic treatment and the metal behaves pretty much as before. The implication is that Mn would be suitable for alloying with Zn.

The corrosion of Co in KOH was also investigated. Since the currents were low and unsteady, it was not possible to obtain a meaningful current-potential curve. The electrode did not tarnish but the rest potential was very sensitive. Probably this potential was controlled by air films of Co oxides ($\sim$ +0.25 v) but when these had been reduced (after a few minutes at +0.3 v), minor contamination with oxygen in the solution was able to control the potential at much higher values (+ 0.98 v). Co appears promising for alloying with Zn.

The corrosion of Fe in KOH was investigated and the passive current was found to be very low, although erratic. Alloying of Zn with Fe may, therefore, reduce the passive corrosion rate of Zn.

c) Passivation Studies with Zn Alloys

1. Passivation of Zinc-Magnesium Alloys

Magnesium has good corrosion resistance in alkaline solutions (Fig. 19) and an alloy of 97 Zn - 3 Mg (wt%) was therefore tested in KOH. Figure 24 compares curves in 1N KOH (stirred) for Zn and 97 Zn - 3 Mg.

The dissolution of the Zn-Mg is similar to Zn but about three times less. An important characteristic of this system is not only the low passive corrosion rate but also the ready activation on demand. Zn in both 1N and 6N KOH readily activates either under cathodic galvanostatic driving or on open circuit. The cathodic chronopotentiogram thus taken has a delay corresponding principally to the reduction of dissolved zincate. To test the suitability or otherwise of the Zn-Mg system in this respect, we carried out the following experiment. The electrode was left at + 1.2 v, well into the

- 48 -
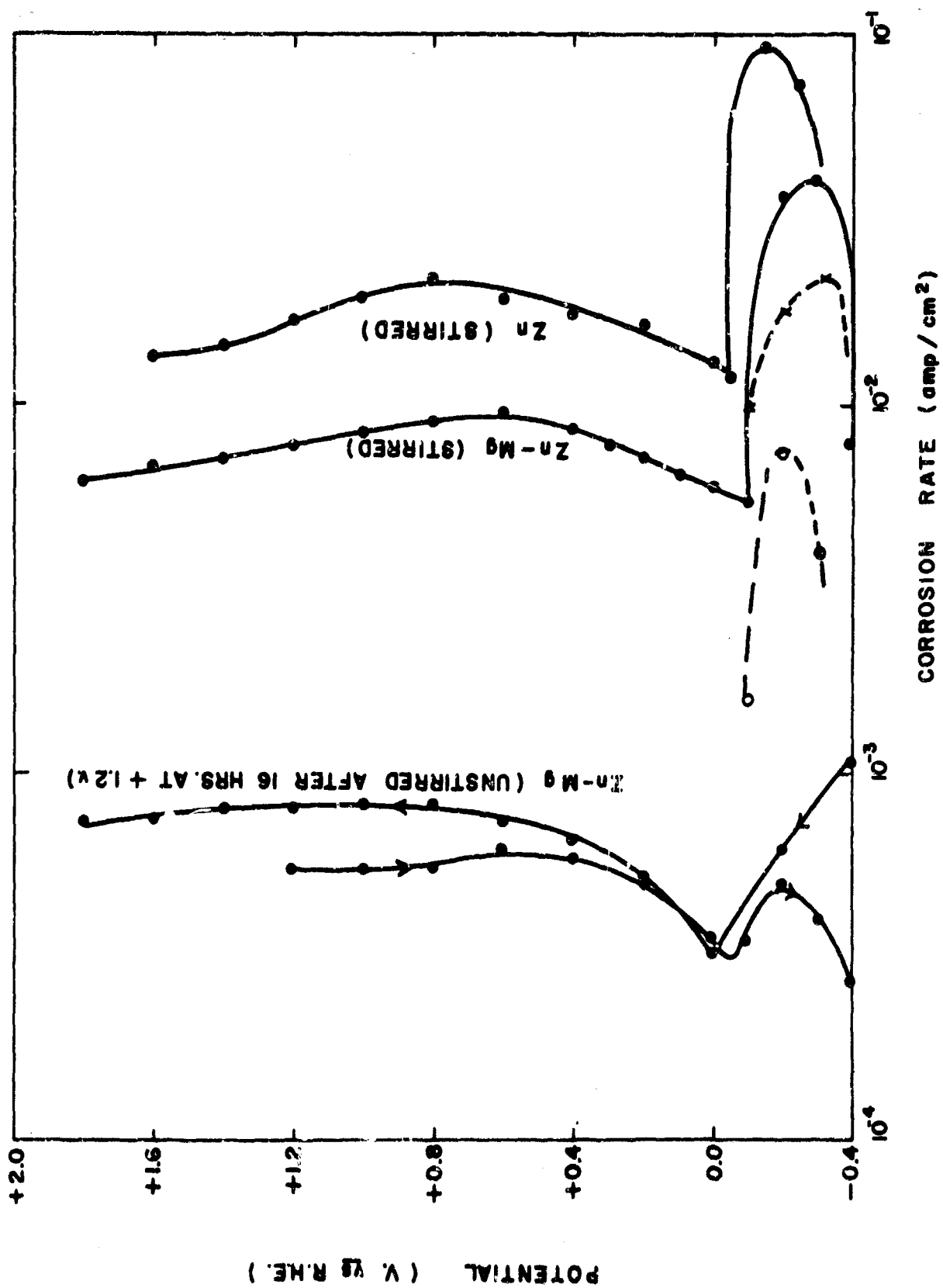
Fig. 24. Corrosion of Zn and 97 Zn - 3 Mg in N KOH at 30°C

passive region, without stirring (Fig. 24). During this time ($\sim$ 16 hours), the current fell from 7.9 mA/cm^2 (stirred) to 0.56 mA/cm^2 (unstirred). Then the oxidation rate of the electrode was studied as before and the electrode, which was black, was inactive as shown in Fig. 24. Although the open circuit potential was still in the zinc dissolution region ($\sim$ 0.37 v) and was rapidly attained on breaking the circuit, it was not possible to activate this electrode again either by vigorous H_2-evolution (attempting to reduce the passive film) or by vigorous O_2-evolution (attempting to reach the transpassive region). In fact, the passive layer behaved like an ohmic film with a resistance (measured with a current interrupter) of about 21.5 .

In a subsequent experiment the electrode was repolished and run through the active dissolution regime (unstirred) as shown in Fig. 24 (crosses). Then, we waited 45 min. at 0.1 v, which is the beginning of the passive region. During this time (5 min. to 45 min) the current fell from 10 to 8.3 mA/cm^2. The aim of this experiment was to investigate just where in the passive region the black ohmic layer is produced. Subsequently, the electrode was rather inactive (even after 10 mA/cm^2 of H_2-evolution for 20 min.); for example, the maximum dissolution rate of the alloy was down to 7.5 mA/cm^2 from 22 mA/cm^2 (unstirred) and extended for a range of less than 0.1 v (in the vicinity of - 0.2 v vs. R.H.E.) Such a curve, taken in the active dissolution region of the alloy, is shown dotted in Fig. 24 (open circles). Repetition of this procedure lowered the maximum dissolution current to 4 mA/cm^2. From this experiment it appears that deactivation of Mg-Zn occurs even as low as - 0.1 v vs. R.H.E.

Reactivation of the alloy by cathodic galvanostatic pulses was attempted. Such activation is possible, although it did not remove the loose black material covering the surface. The possibility of zinc plating from solution onto the alloy electrode during the cathodic pulse was considered, and it was concluded that it did not affect the results appreciably. Therefore,

activation is not due to oxidation of Zn plated out from the solution during the cathodic "activation". We are sure of this because the extra charge due to active dissolution at say - 0.3 v is much larger than could be accounted for by plated zinc. For example, after one minute of a cathodic activation at - 1 mA, no more than 60 mcoul of Zn could be plated onto the electrode. (This assumes no H_2-evolution; there is some however.) This is then the maximum excess charge which could be attributed to plated zinc in subsequent oxidation of the alloy. In practice, we find at least 1200 mcoul (Fig. 25). Cathodization for longer times gives a more long-lived activation.

It is evident that we are partially reducing a very refractory surface layer which is forming at the active dissolution potential and that this cannot be the black and rather porous-looking layer which the electrode acquires after some time under active dissolution. Deactivation of the corrosion, both in the "active" dissolution potential region (Fig. 26) and in the subsequent "passive" region, evidently occurs because of formation of a surface layer which is difficult to remove. Presumably, this is complicated by loss of zinc from the surface layers, but it is not certain that this is a predominant effect. The Mg-Zn solid solution system does not look very promising because the presence of Mg seems to limit the active dissolution of Zn rather more than it lowers the passive current.

2. Passivation of Zinc-Copper Alloys

Cu has good corrosion resistance to 1N KOH (Fig. 20) and therefore its alloys with Zn were tested.

Fig. 27 shows the dissolution of 67-33 Zn in 1N KOH. The passive current is about ten times higher than that of Cu. After 17 hours at 1.2 v, this decreased to 15 μA/cm^2 and the electrode became black. The electrode was fairly readily activated but, as can be seen from Fig. 27, the over-all behavior does not show the Zn active dissolution region.
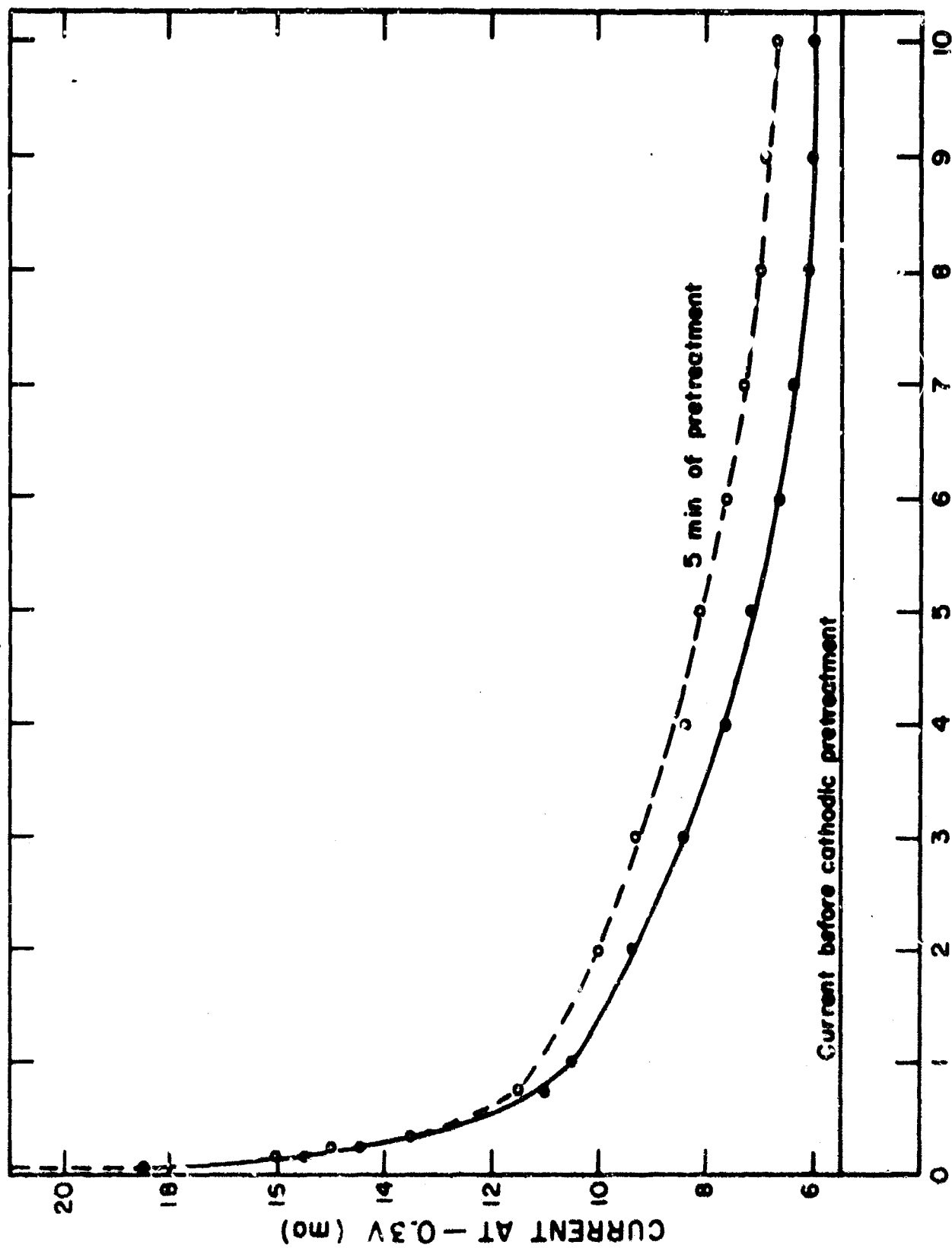
Fig. 25.   Anodic Dissolution of 97 Zn – 3 Mg in 5N KOH at 30°C, unstirred

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Fig. 26. Anodic Dissolution of 97 Zn - 3 Mg in 6N KOH at 30°C, unstirred

Fig. 27. Anodic Dissolution of 67 Cu - 33 Zn in 1N KOH at 30°C, unstirred

CORROSION RATE (amp./cm.^{2})

POTENTIAL (V. vs. R.H.E.)

The corrosion of 80 Zn - 20 Cu (wt %) in 1N KOH is shown in Fig. 28. This curve shows currents taken point by point after 5 minutes at each potential. The currents were fairly steady; e.g. at - 0.2 v there is no change from 1 min to 5 min and between 0.5 and 0.7 v, the worst region, it decreased by $<$ 50% in this time range. The diagram shows that the active dissolution of Zn has been pushed from $\sim$ - 0.3 v to $\sim$ 0.1 v and that the critical current is $\sim$ 10 mA/cm^2 (vs. $\sim$ 60 mA/cm^2 for pure Zn at 0.3 v). This undoubtedly reflects the lowering of Zn "activity" in the alloy. After the first passivation at $\sim$ 0.3 v, the electrode shows another active peak at 0.55 v and another at 0.85 v. Another peak is seen at 1.1 v. This complex corrosion behavior cannot be fully accounted for at this time and it appears inappropriate to investigate the system more fully in this context. The lowest passive current is at $\sim$ 1.0 v; this is 1.7 mA/cm^2 after 5 min and still 0.9 mA/cm^2 after 17 hours.

The conclusion from these studies is that Cu-Zn alloys do not have suitable corrosion properties for the primary reserve battery. This is because the effect of the added Cu is both to raise the active dissolution poten-tial of the Zn and to decrease its critical current, not to lower its passive current enough.

As an alternative to alloying Cu with Zn, we considered briefly the possibility of protecting the Zn by plating Cu onto it. In this configuration the Zn electrode would be stored Cu-plated. Cu does not corrode at open circuit once O$_2$ in this electrolyte has been consumed. To activate the battery a pulse is applied to dissolve Cu. One possible disadvantage of this procedure is that it could not be used for porous Zn (high rate) anodes, only for smooth ones. Another possible problem is that in order to protect the Zn we might have to put a large thickness of Cu onto the Zn (e.g. say microns). This would make activation difficult. Even worse, once the Cu had been removed during the activation procedure, it might plate back onto the Zn, which will now be well negative of the Cu reversible potential ($\sim$ +0.55 v).

To test this notion, we attempted to plate Cu onto Zn. The minimum successful plate used so far involves about 1 coul/cm^2 from a cyanide bath and about 10 coul/cm^2 from an acid sulfate bath
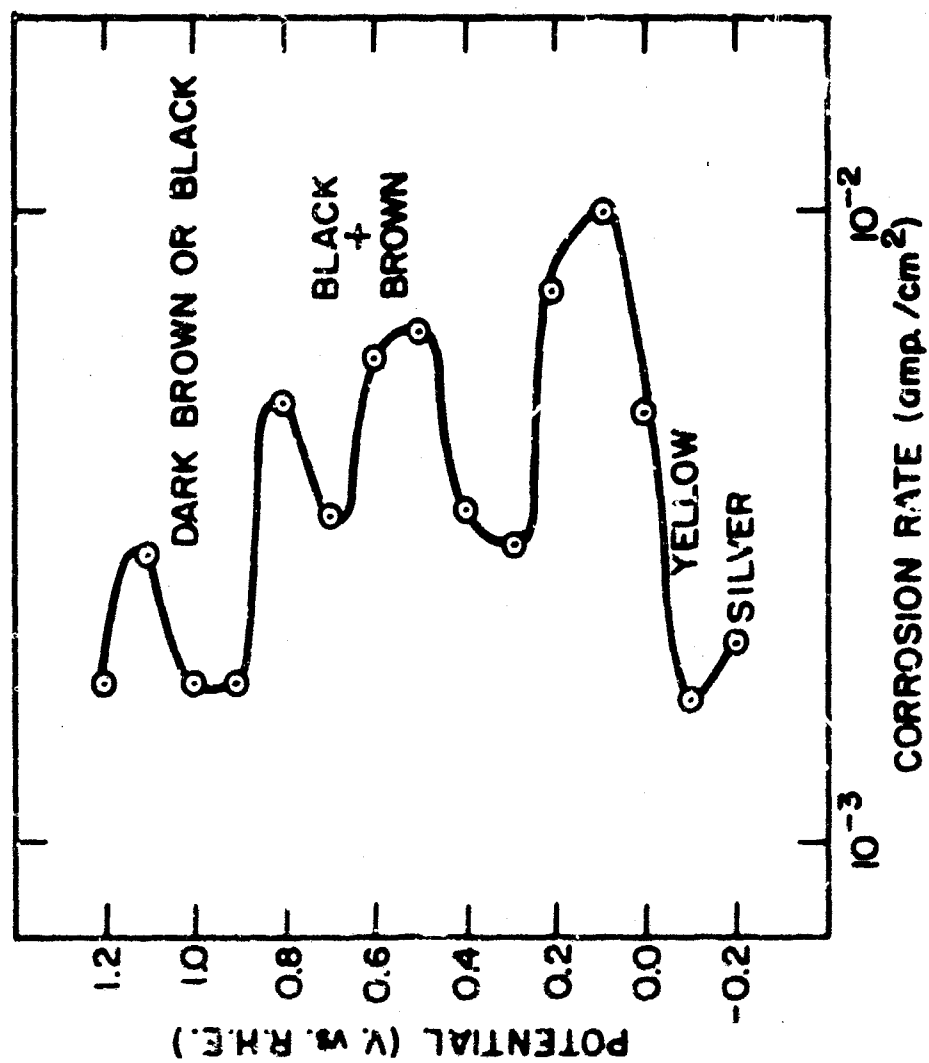
Fig. 28. Anodic dissolution of 80 Zn - 20 Cu in 1N KOH at 30°C, unstirred

(~ 6000 $\overset{o}{A}$ in all). This amount of Cu on Zn gave the Cu potential in 6N KOH. However, although it can be removed by anodic discharge, activation is lengthy because of the large charge involved. Cu, once removed, will tend to plate back onto the Zn thus deactivating it. Thus, the activated Zn could only be used while dissolving very rapidly, e.g. - 0.2 v in 6N KOH. We conclude that further development wi'1 be necessary to make this procedure suitable for the complete protection of Zn anodes.

3. Passivation of Zn-Fe Alloys

Typical current-potential curves for an alloy of 90 Zn - 10 Fe are shown in Fig. 29.

Considerable difficulty was experienced in obtaining alloys free of pores or voids. The difference in behavior between nonporous alloys and alloys containing voids is shown in the figure and is essentially what is expected from differences in surface area.

The curves show an active-passive behavior, but the current in the passive range is substantial (about 20 ma/cm^2 in 6N KOH for a nonporous alloy). The high passive current is somewhat surprising in view of the stability of passive films on iron in alkaline solutions. It appears that approximately 10% of Fe lowers but slightly the passive current (compare to 50 ma/cm^2 for pure Zn in 6N KOH). The critical current is also lowered by addition of iron from about 300 ma/cm^2 for pure zinc to about 40 ma/cm^2 for the 90 Nz - 10 Fe alloy; the current potential curve in the active region is also generally shifted to more positive potentials.

It appears from the above that addition of 10% Fe improves the passive behavior little while it makes the active dissolution characteristics significantly less desirable than those of pure zinc.

4. Passivation of Zn-Mn Alloys

As mentioned previously, Mn appears sufficiently corrosion resistant to KOH to be used as a possible alloying addition for improving the passive behavior of Zn. Results for a nominal composition of 83 Zn - 17 Mn in N KOH are shown in Fig. 30 which gives currents taken at 5 min at
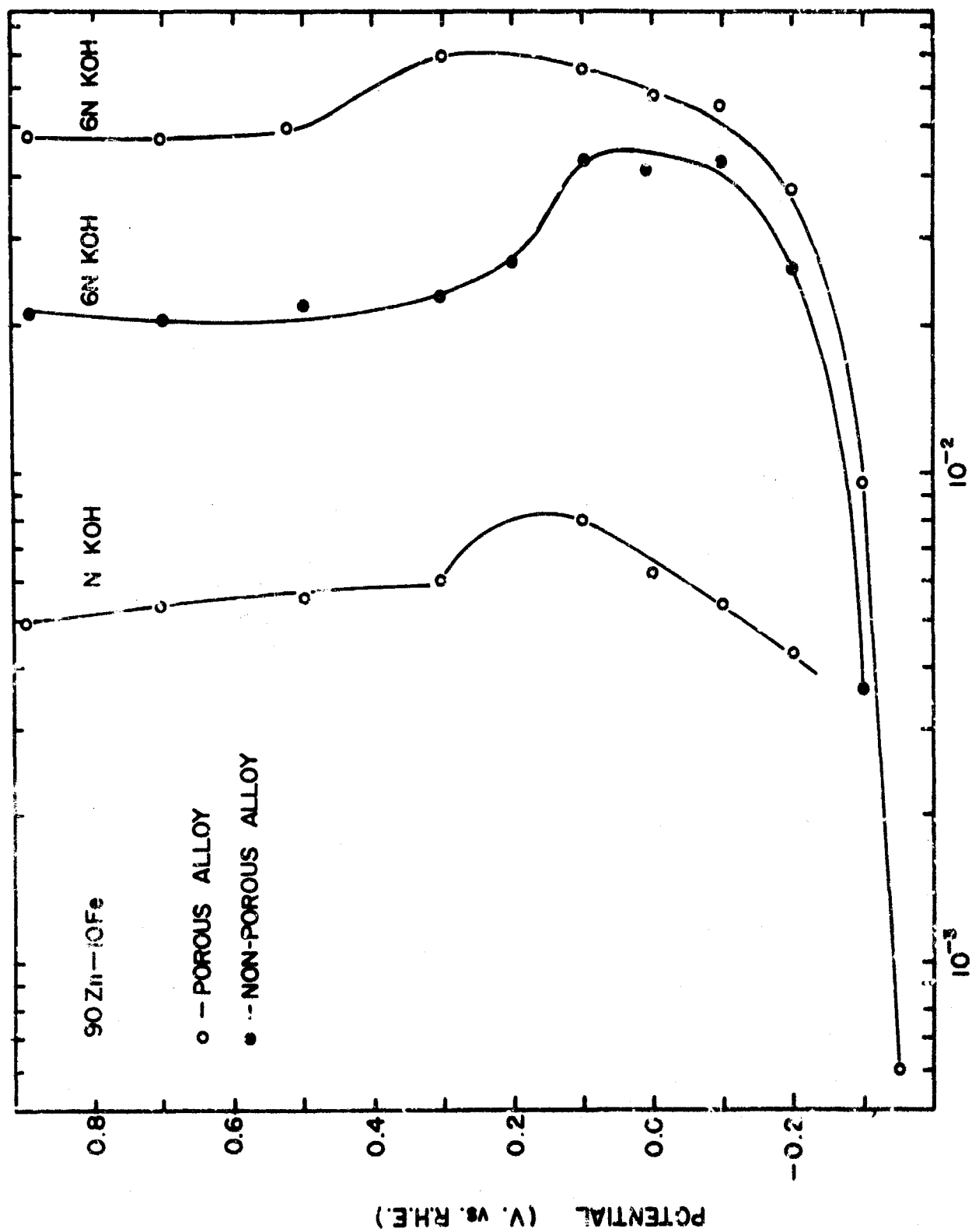
Fig. 29. Anodic Dissolution of 90 Zn - 10 Fe Alloy at 30°C, unstirred

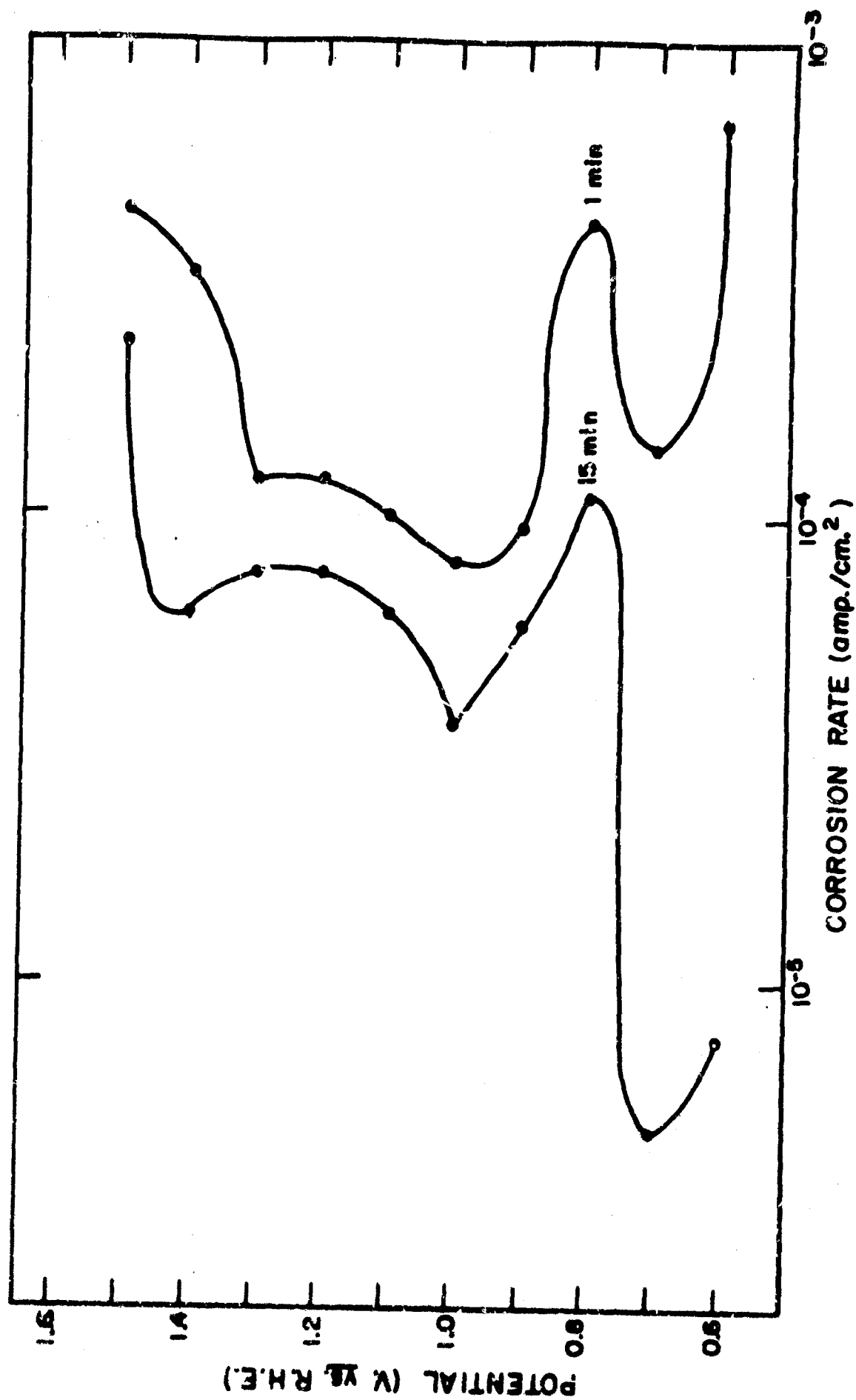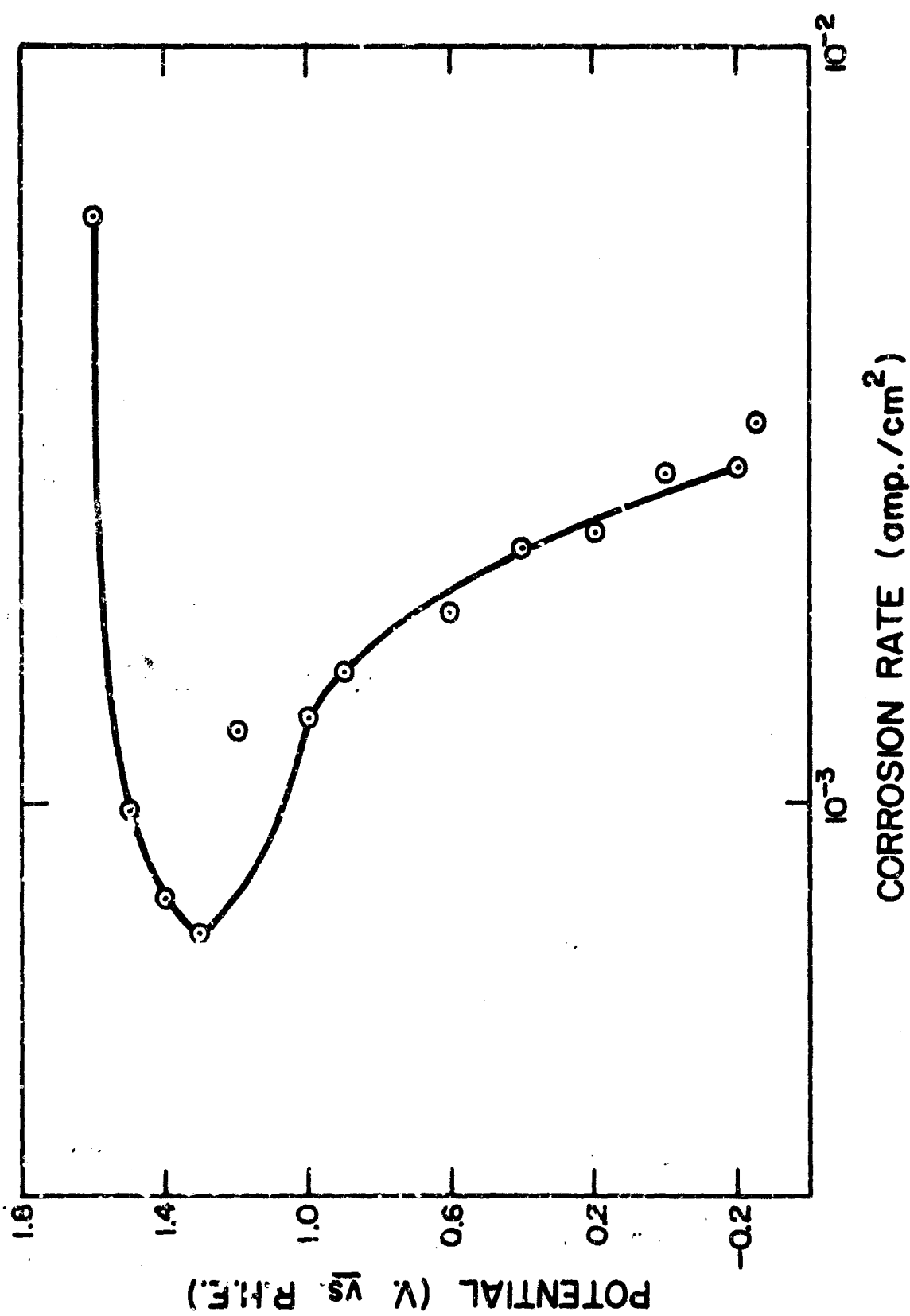Fig. 30. Anodic Dissolution of 83 Zn - 17 Mn in 1 N KOH at 30°C, unstirred.

each potential with a progression up the curve in the usual point-by-point fashion. The currents were fairly steady ($<$ 10% change in 3 to 5 min). The open-circuit potential was -0.30 v $\underline{vs}$ RHE, a little more positive than Zn itself, and the maximum active dissolution current ($\sim$ 3 mA/cm^2) was found at quite low potentials ($\sim$ -0.25 v). Both of these are desirable if we are to maintain the power density of the battery system. However, even at this potential the electrode turned black and at higher potentials a long, gradual passivation was observed. The minimum current ($\sim$ 0.6 mA/cm^2) was too high for the present purpose and also occurred at too high a potential ($\sim$ 1.3 v $\underline{vs}$ RHE, which is too close to the Ag/AgO potential). Although the general character of the corrosion of the Zn-Mn alloy is qualitatively suitable for our purpose, the corrosion rate is too high in the passive region and too low in the active region. Consequently, the material was not tested in 6N KOH.

5. Other Zinc Alloys

The most promising Zn alloys were Zn-Co and Zn-Ni. Their behavior is discussed in detail in the next section.

VII. ZINC-COBALT AND ZINC-NICKEL ALLOYS

a) Passivation of Zn-Co Alloys

Three alloys in the Zn-Co system were studied. Alloys in the γ_1-phase (nominally 11% Co); alloys in the γ-phase (nominally 18% Co); and alloys in the β_1-phase (nominally 44% Co).

1. Alloys in the γ-phase

The nominal composition of these alloys was 82Zn-18Co. Chemical analyses showed 82.3Zn and 17.3Co for one set of alloys and 87.8Zn and 21.6Co for another.

The current-potential curve for this alloy is shown in Fig. 31. The rest potential was about 0.15 v vs RHE, somewhat higher than Zn, but active dissolution occurred at a reasonably low potential. Thus the critical current of ~7.5 mA/cm^2 was found at ~0.0 v vs RHE.

Below this potential some H$_2$-evolution was observed. This means that the actual corrosion rates in this region are higher than those shown in Fig. 31. A separate experiment on a fresh sample which had not been passivated showed that H$_2$-evolution at open circuit (-0.15 v) is about 300 μA/cm^2, and while this undoubtedly varies with the state of the surface, it does not cause a serious error in the data of Fig. 31.

The current-potential curve of Fig. 31 is most promising: the critical current is reasonably high and the passive current is interestingly low (~150 μA/cm^2)and observed over a wide range of potential (0.2 to ~1.5 v). After 15 hours at 0.8 v, the passive current fell to 55 μA/cm^2. For Zn itself in 1N KOH, i_c is ~35 mA/cm^2 and i_p is ~4.5 mA/cm^2. The ratios of the critical currents (the maximum current we can draw from the anode) in going from Zn to the alloy is ~0.22, while the ratio of passive currents is ~0.012. Thus, we have only depressed i_c by a factor of 5 but we have lowered i_p by about 80 times. The Co-Zn system is evidently approaching the desired behavior for a passive-reserve battery, although its passive current is still too high.
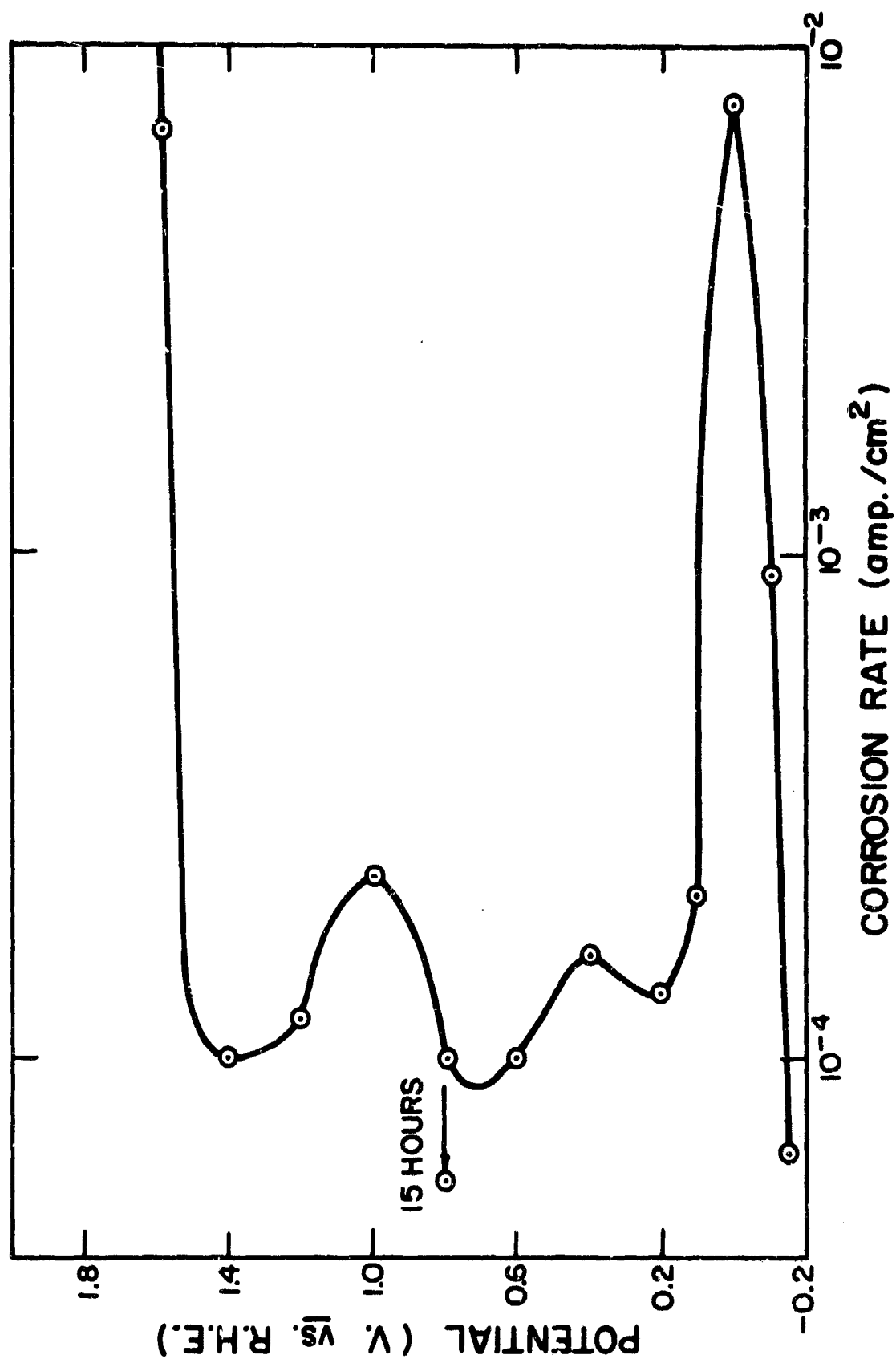
Fig. 31. Anodic Dissolution of 81 Zn - 19 Co in 1 N KOH at 30°C, unstirred.

After 15 hours at 0.8 v, the electrode was black and difficult to activate. After 64 hours at 0.2 v, the electrode was black and shiny and the passive current was 56 $\mu A/cm^2$. H_2-evolution occurred on this black layer when a cathodic pulse was applied, and complete activation of the electrode with cathodic pulses did not appear possible. Thus at 0.0 v, the current was only $\sim$1.3 mA/cm^2 (as against $\sim$7.5 mA/cm^2 for the original specimen).

In 6N KOH, the 78 Zn - 22 Co alloy also showed promising behavior (Fig. 32). The rest potential was - 0.16 v and a separate experiment showed that H_2-evolution at open circuit was 1.0 mA/cm^2. The current in the active dissolution region ($<$ 0.0 v) was quite steady but above this, fell with time. The data in Fig. 32 are for currents taken point-by-point after 5 min at each potential. At 0.1 the electrode became black and remained so subsequently. The critical current is 110 mA/cm^2 (vs. 350 mA/cm^2 for Zn, a ratio of 0.31), and the passive current (after 15 hours at 0.2 v) is 0.21 mA/cm^2 (vs. 55 mA/cm^2 for Zn, a ratio of 0.004). Thus the alloy is much better than Zn and better, relatively, than 1N KOH. The passive current is now, of course, too large (210 $\mu A/cm^2$) for use in the passive reserve mode.

Galvanostatic activation was attempted after potentiostating in the passive region (+ 0.2 v). After 30 min at 0.2 v, a black layer formed on the electrode which was partially reduced during a - 150 mA/cm^2 charging current. The remainder peeled off when H_2-evolution was reached. The current at 0.0 v was 63 mA/cm^2 as against the original 110 mA/cm^2. Subsequent alternate treatments of +0.2 v and - 150 mA/cm^2 led to further deactivation, viz. current of 33 and 9 mA/cm^2. Attempted activation after 15 hours at 0.20 v (during which the current went down to 210 $\mu A/cm^2$) was quite successful, viz. 1.5 $coul/cm^2$ at - 300 mA/cm^2 yields a current of 20 mA/cm^2 at 0.0 v. A further 3 $coul/cm^2$ activated the electrode to 29 mA/cm^2. These results are summarized in Table II.

Thus, the 78 Zn - 22 Co alloy is reasonably promising in KOH solutions in that its passive current is approaching the desired level, its i_c/i_p ratio ($\sim$ 500:1 in 6N KOH) is also approaching an acceptable level, and it can be activated to a considerable extent, at
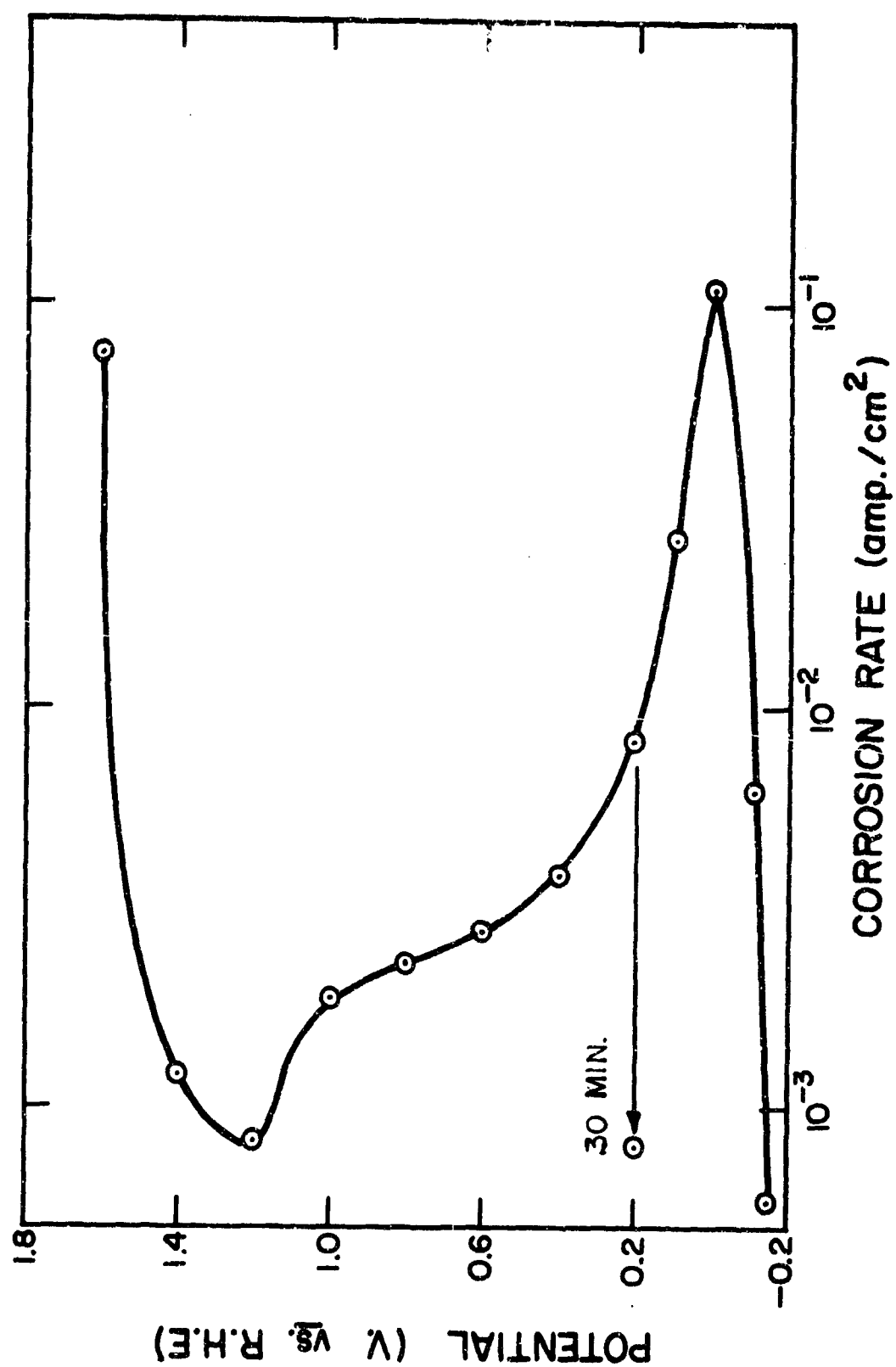
Fig. 32. Anodic Dissolution of 78 Zn - 22 Cc in 6 N KOH at 30°C, unstirred.

Table II

Activation of 77.8 Zn - 21.6 Co Alloy
6N KOH at 30.0°C in N_2-Saturated Solutions

		Current (ma/cm^2)		
I. Passive Potential		1 min	3 min	5 min
+0.20 v		+30	9.6	7.5

Activate by 300 ma/cm^2 cathodic pulse for 20 sec.

	10 sec	30 sec	60 sec	120 sec
Current at 0.0 v	2.7	1.1	1.1	2.1 ma/cm^2
% Activation	29%	14.5%	14.5%	27%

	Current (ma/cm^2)
II. Passive Potential	30 min
+0.20 v	1.4 ma/cm^2

Activate by 300 ma/cm^2 cathodic pulse for 30 sec.

	10 sec	30 sec	60 sec	120 sec
Current at 0.0 v	48	54	72	69 ma/cm^2
% Activation	50%	56%	75%	72%

	Current (ma/cm^2)
III. Passive Potential	30 min
+0.20 v	1.1 ma/cm^2

Activate at -0.3 v ($\sim$360 ma/cm^2 cathodic) for 30 sec.

	10 sec	30 sec	60 sec	120 sec
Current at 0.0 v	78	72	75	75 ma/cm^2
% Activation	70%	65%	68%	68%

Table II (Cont.)

$$\text{Current (ma/cm}^2\text{)}$$

IV. Passive Potential	30 min

+0. 2 v

Activate at - 0. 25 v ($\sim$ 210 ma/cm^2 cathodic) for 30 sec.

	10 sec	30 sec	60 sec	120 sec
Current at 0.0 v	45	42	57	60 ma/cm^2
% Activation	45%	42%	57%	60%

$$\text{Current (ma/cm}^2\text{)}$$

V. Passive Potential	15 min
+0. 2 v	1. 4
+0. 8 v	2. 6
+1. 2 v	1. 2

Activate at -0. 3 v ($\sim$ 300 ma/cm^2 cathodic) for 30 sec.

	10 sec	30 sec	60 sec	120 sec
Current at 0.0 v	54	48	48	54 ma/cm^2
% Activation	52%	46%	46%	52%

$$\text{Current (ma/cm}^2\text{)}$$

VI. Passive Potential	30 min
+0. 2 v	1. 4 m

Activate at -0. 3 v ($\sim$ 420 ma/cm^2 cathodic) for 30 sec.

	10 sec	30 sec	60 sec	120 sec
Current at 0.0 v	75	69	69	75 ma/cm^2
% Activation	66%	61%	61%	66%

least in 6N KOH. The passive current is probably controlled by the solubility of the appropriate passivating film and it may be possible to limit this by additions to the electrolyte.

2. Alloys in the γ_1- phase

An alloy with a nominal composition of 89 Zn - 11 Co, which corresponds to the γ_1- phase of the Zn-Co system, was also studied. Polarization curves for this alloy are shown in Fig. 33.

A typical active-passive transition is observed in N KOH at about +0.1 v and 15 mA/cm^2; in 6N KOH, the critical potential and current are 0.0 v and 250 mA/cm^2, respectively. The currents are extremely steady; generally, the current at the end of 3 min was the same as that after 30 min at any given potential. Even for long times, no appreciable change in the current is observed; (e.g. after 15 hours at 1.2 v in N KOH, the current changed from 4.0 to 5.0 x 10^{-4} amp/cm^2).

Activation of the 89 Zn - 11 Co alloy was relatively easy even in N KOH. Starting at 1.2 v (passive current 5.0 x 10^{-4} amp/cm^2 after 15 hrs), a cathodic pulse of 300 mA/cm^2 was applied. The visible oxide layer "peels off" and the passive layer is presumably also reduced. The potential was stepped to zero after 15 sec, and the current observed as a function of time: It is initially higher than in the steady state and slowly drops to the values given in Fig. 33. For example, after 1 min at 0.0 v, the current was 19 mA/cm^2; after 2 min, 15 mA/cm^2. These values are to be compared with the steady-state value of 11 mA/cm^2 given in Fig. 33.

Although the passive characteristics of the 89 Zn - 11 Co alloy are much improved over those of pure zinc, the passive currents in both N and 6N KOH are too large for the intended application.

3. Alloys in the β_1-phase

Homogeneous alloys containing approximately 44% Co (β_1-phase) were prepared in sealed, quartz ampules which prevented the loss of Zn.

The anodic polarization curve of the β_1-phase in 6N KOH is shown in Fig. 34.
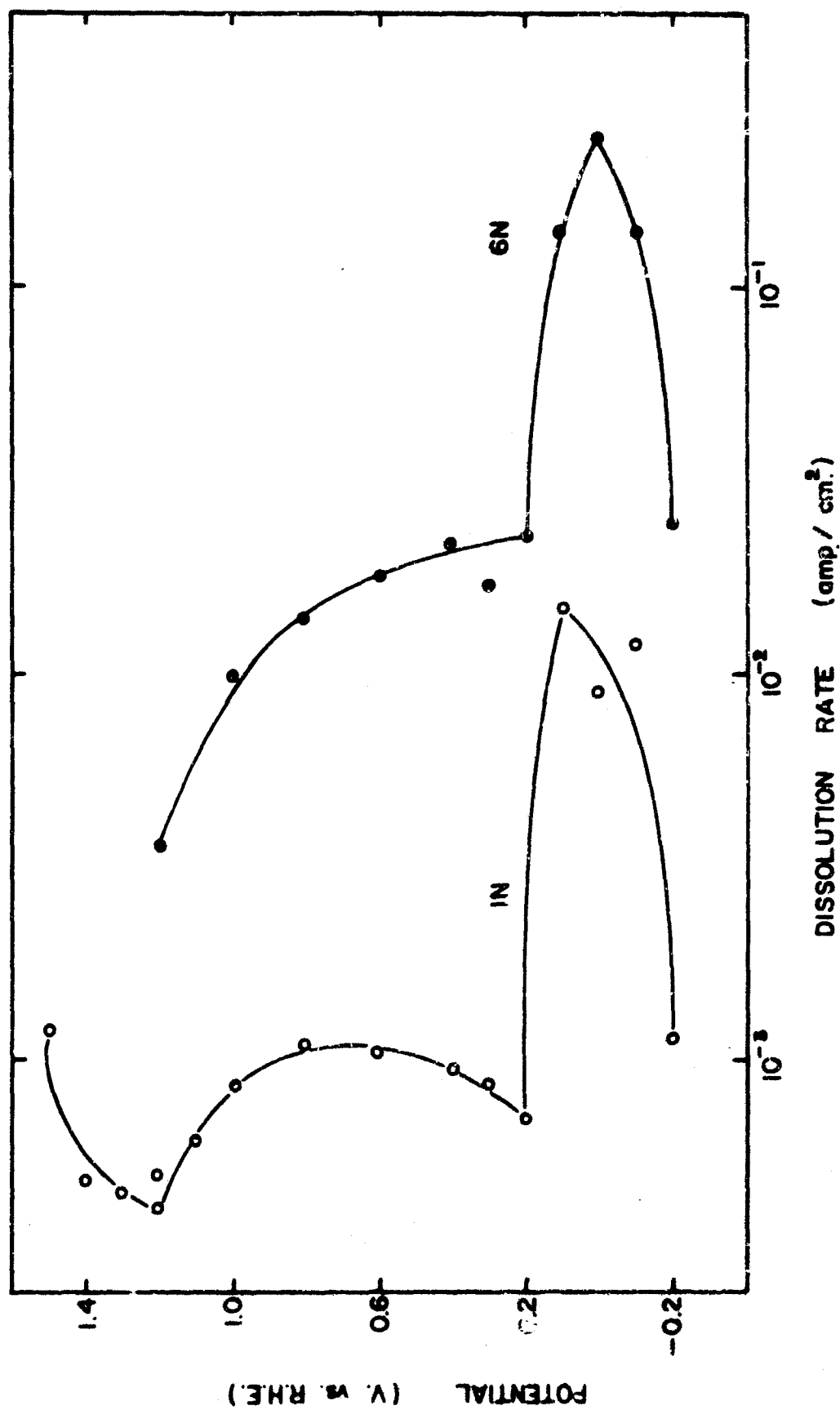
Fig. 33. Anodic Dissolution of 89 Zn - 11 Co in KOH at 30°C, without stirring

The anodic polarization curve of the 44% Co alloy has been uniformly shifted to lower currents in comparison to that of the 18% Co. This is true both in the active and the passive potential regions. The long term (16 hrs) currents are about ten times smaller. We see, therefore, that increasing additions of Co improve the passive characteristics, a result which was expected. However, Co also decreases the active current and shifts the critical potential by 50 mv in the positive direction. The passive current decreased by a factor of 6.1 while the current density in the active region decreased by a factor of 3.5.

4. Long-Term Passivation Behavior

The long term behavior of an alloy containing 18% Co (γ -phase) is shown in Fig. 35. The electrode was polarized as before from the active region to 0.6 v and kept at this potential over the next 64 hrs. The passive current decreased from its usual value of 3 ma/cm^2 at the end of 5 min. to 1 ma/cm^2 in about 20 hrs. Beyond this time, it increased again and reached a steady state which was not much different from the 5 min. value, viz. 3 ma/cm^2. This result was somewhat surprising since, in general, one expects a more or less exponential decay to a final steady value. The type of curve obtained is probably due to roughening of the electrode because of the relatively high dissolution rates. The high dissolution rate is, of course, due to the relatively high solubility of the passive layer in 6 N KOH.

5. Summary of Zn-Co Alloys

Alloys with low Co content (~11%) corrode at too high a rate in the passive region; alloys with high Co content (~ 44%) corrode at a low rate, but are difficult to activate. Intermediate Co contents (~20%), yield relatively low corrosion rates in the passive region and alloys which can be activated relatively easily. However, the passive corrosion current on 6N KOH is still higher than an acceptable maximum by about an order of magnitude.
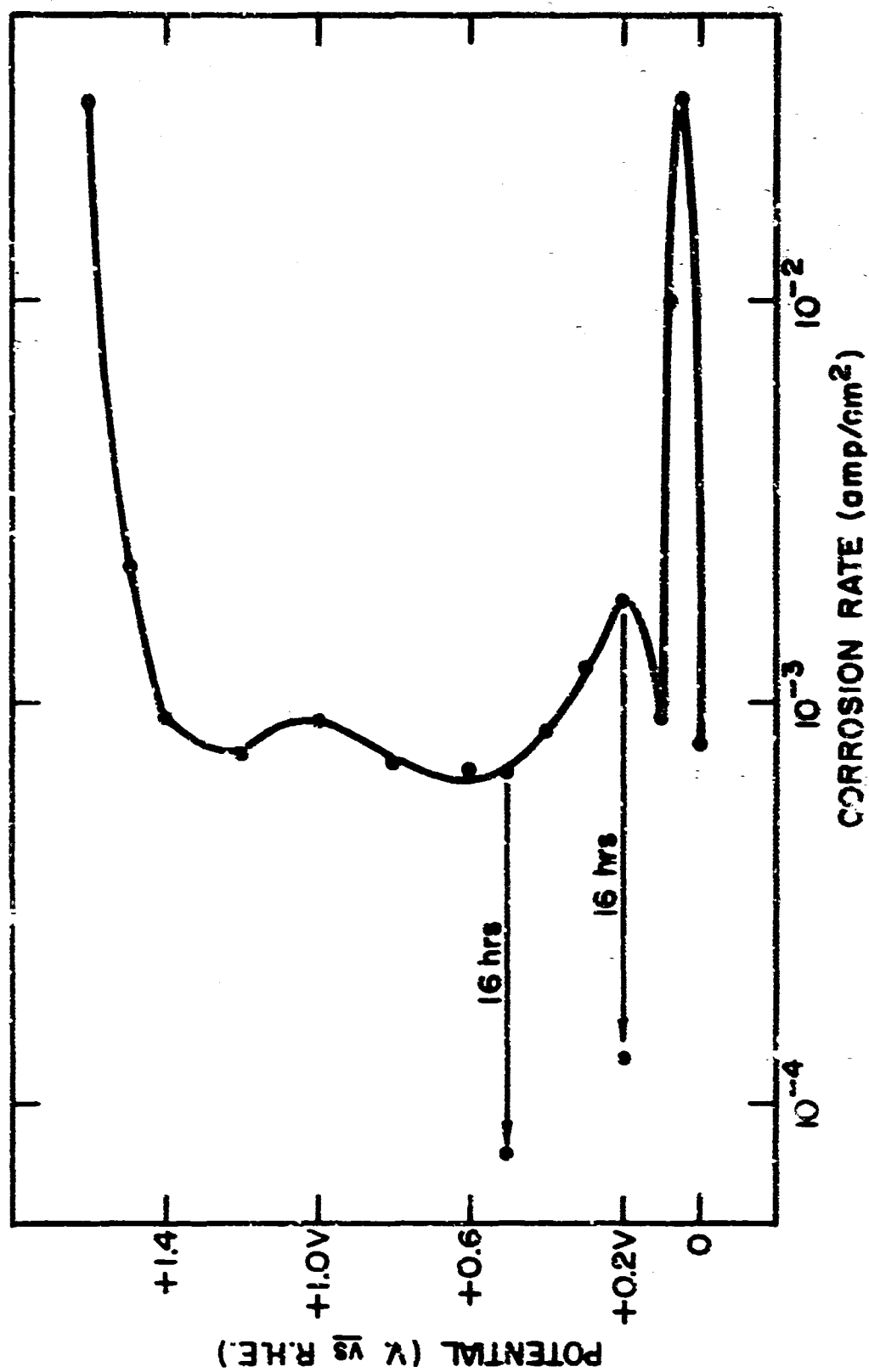
Fig. 34. Anodic Polarization Curve for 44% Co-Zn in 6 N KOH at 30°C, unstirred.
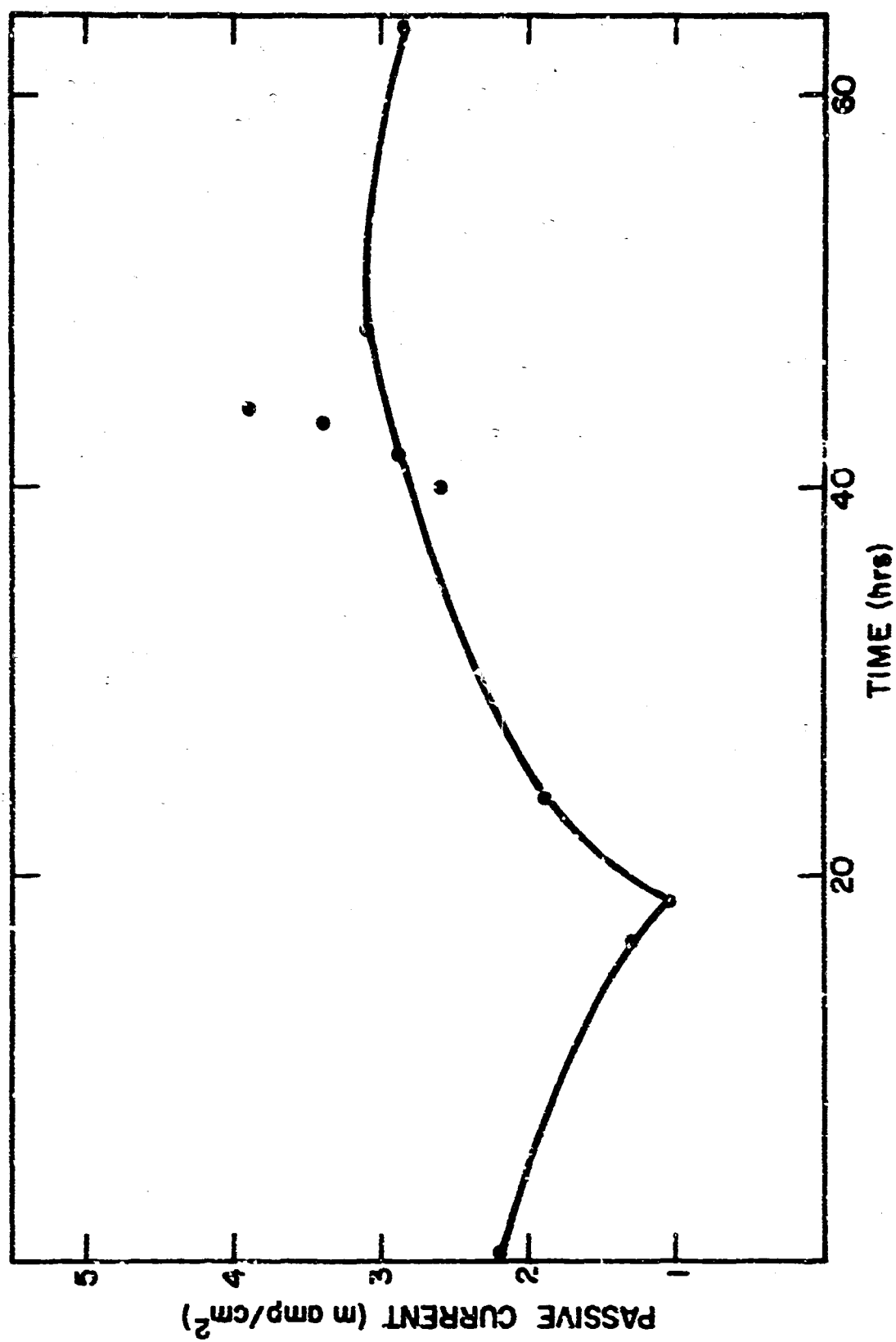
Fig. 35. Passive Current at 0.6 v for 19% Co-Zn in 6 N KOH at 30°C, unstirred

b) Passivation of Zn-Ni Alloys

It is known that Ni has good corrosion resistance to alkaline solutions, and therefore, we carried out an examination of the corrosion of Zn-Ni alloys.

1. Alloys in the γ-phase

The nominal composition of these alloys was 80% Zn - 20% Ni. Chemical analyses showed 19 to 21%, the balance being Zn.

Figure 36 shows the current-potential curve (10 min points) for 80 Zn - 20 Ni in 6N KOH. The open circuit potential was - 0.135 v. The currents in the active region were fairly steady; e.g. at 0.1 v there was <10% change from 1 min to 5 min. In the passive region the decay of current was greater and at 0.7 v, for example, the current fell 40% from 1 min to 5 min and another 30% from 5 min to 10 min. The active dissolution of the alloy is quite good ($i_c \sim 50$ mA/cm^2) although not quite as good as the Co alloy in 6N KOH (Fig. 32) and at a higher potential (+0.1 v vs 0.0 v). The electrode became black in the active region and some H$_2$ was evolved. Examination of the surface showed that this evolution appeared to occur on specific parts of the surface, perhaps at grain boundaries.

After 15 hours at 1.0 v, the passive current fell to 80 μA/cm^2, which is ~1/3 of that for the Co alloy in 6N KOH (210 μA/cm^2). The critical current for the alloy (50 mA/cm^2) was 0.14 that of Zn in 6N KOH and the passive current was ~ 0.0014 that of Zn. The ratio of i_c/i_p (600:1) is a little better than that of the Co alloy.

The anodic behavior of the 80 Zn - 20 Ni alloy in 1, 3, and 6N KOH at 30°C is shown in Fig. 37. The critical potential (vs RHE) is essentially independent of the KOH concentration. In other words, it shifts to more noble values in the same way as the reversible hydrogen electrode (~60 mv per unit change in activity of KOH). The critical current increases with KOH concentration from about 6.0 mA/cm^2 in N KOH to 50 mA/cm^2 in 6N KOH. The passive current also increases with KOH concentration from about 0.055 mA/cm^2 in N KOH at 0.25 mA/cm^2 in 6N KOH.

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CORROSION RATE (amp./cm²)

POTENTIAL (V. vs. R.H.E.)
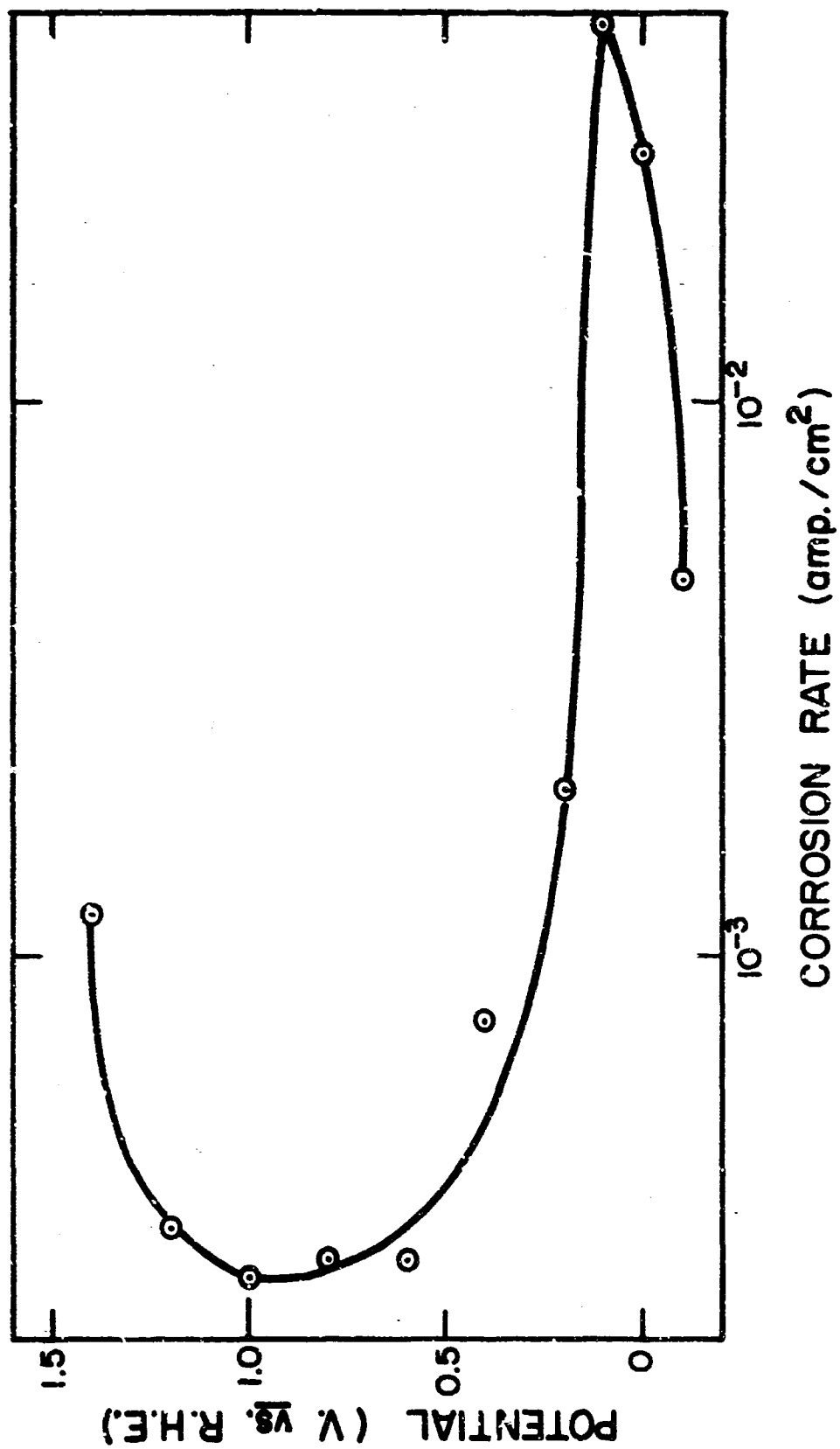
Fig. 36. Anodic Dissolution of 80 Zn - 20 Ni in 6 N KOH at 30°C, without stirring.
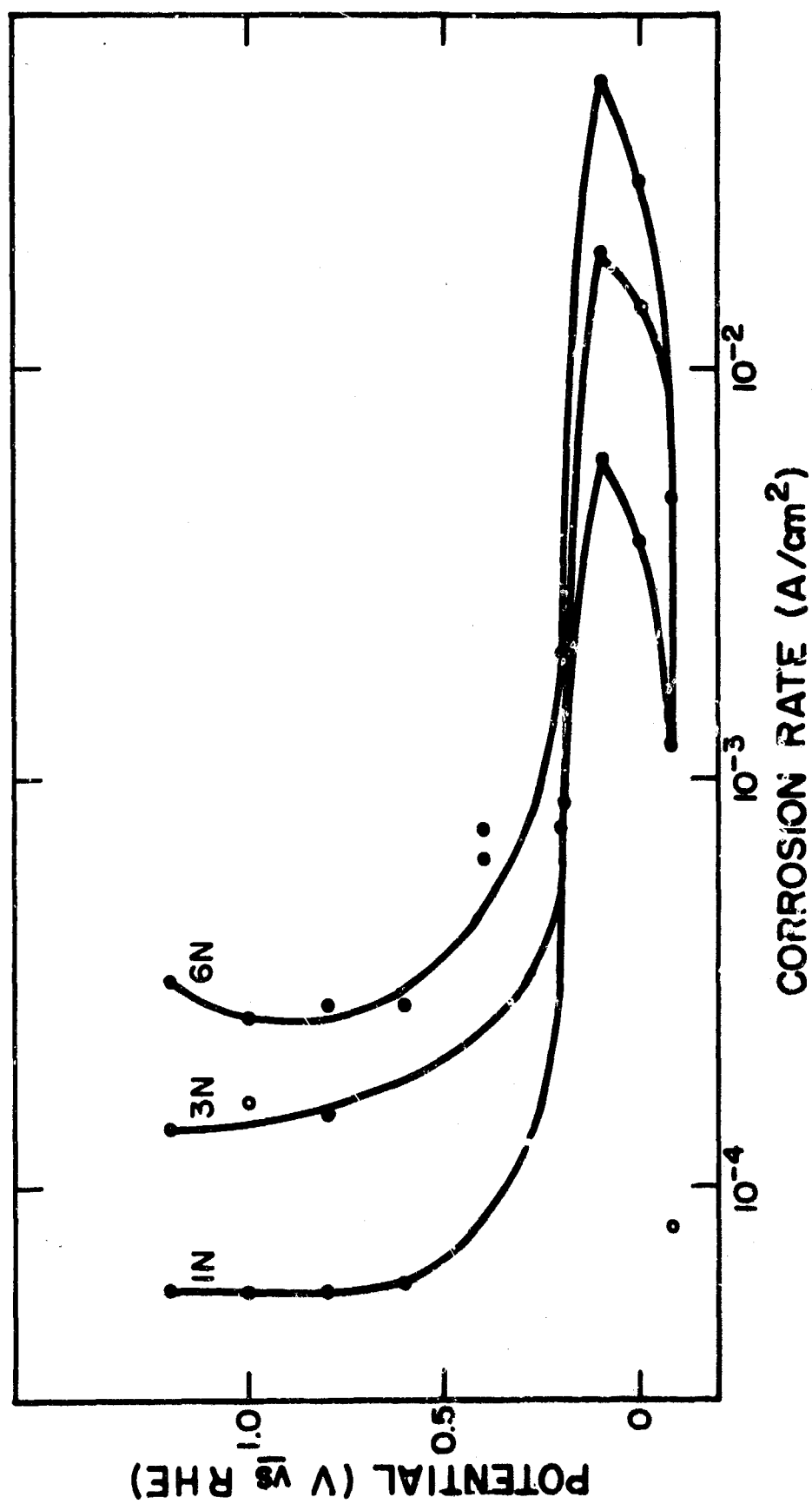
Fig. 37. Anodic Dissolution of 80 Zn - 20 Ni in KOH at 30°C, without stirring

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As mentioned above, the passive currents are time-dependent, while the currents in the active region are not. For example, in 6N KOH the passive current decreases from the value given above (250 μA/cm^2) to 80 μA/cm^2 in 15 hrs. In N KOH and at a fixed potential of 0.80 v, the passive current decreases from 55 μA/cm^2 to 32 μA/cm^2 in 16 hours (see below).

It should be pointed out that, in general, the passive current is expected to decrease as a function of the logarithm of time. This is because the passive film thickens according to a direct logarithmic relation for most metals and alloys.

Activation of 80 Zn - 20 Ni Alloys

The activation characteristics of passivated 80 Zn – 20 Ni alloys in N KOH were studied in detail. Cathodic chronopotentiograms, obtained at a cathodic current density of 200 mA/cm^2, are shown in Fig. 38 for alloys passivated at 0.8 and 1.2 v. It is evident that no reduction plateau exists for alloys previously passivated at 0.8 v, while a very distinct potential arrest appears with alloys passivated at 1.2 v. Since it is clear from the anodic curve that a passive film is present at 0.8 v, we conclude that the passive layer formed at relatively low potentials is difficult to reduce. On the other hand, the passive film formed at higher potentials is apparently more easily reducible.

Similar results were observed in 3N KOH. In 6N KOH a potential plateau, corresponding to oxide reduction, is apparent after passivation both at 0.8 and 1.2 v.

Preliminary experiments showed that it was relatively difficult to activate alloys in 1 and 3N KOH by cathodic pulses of the order of 200 mA/cm^2. Accordingly, the activation characteristics were studied in 6N KOH.

Figure 39 presents results on the activation of 80 ZN - 20 Ni in 6N KOH solutions. In each case the electrode was passivated first at 0.5 v until the passive current density was 300 μA/cm^2 (generally requiring about 15 min), then the potential was increased to values between 1.45 and 1.6 v for 60 sec, and then it was lowered to 0.0 v vs RHE and the current observed as a function of time. Figure 39 shows the ratio of the current obtained after the sequence described above,
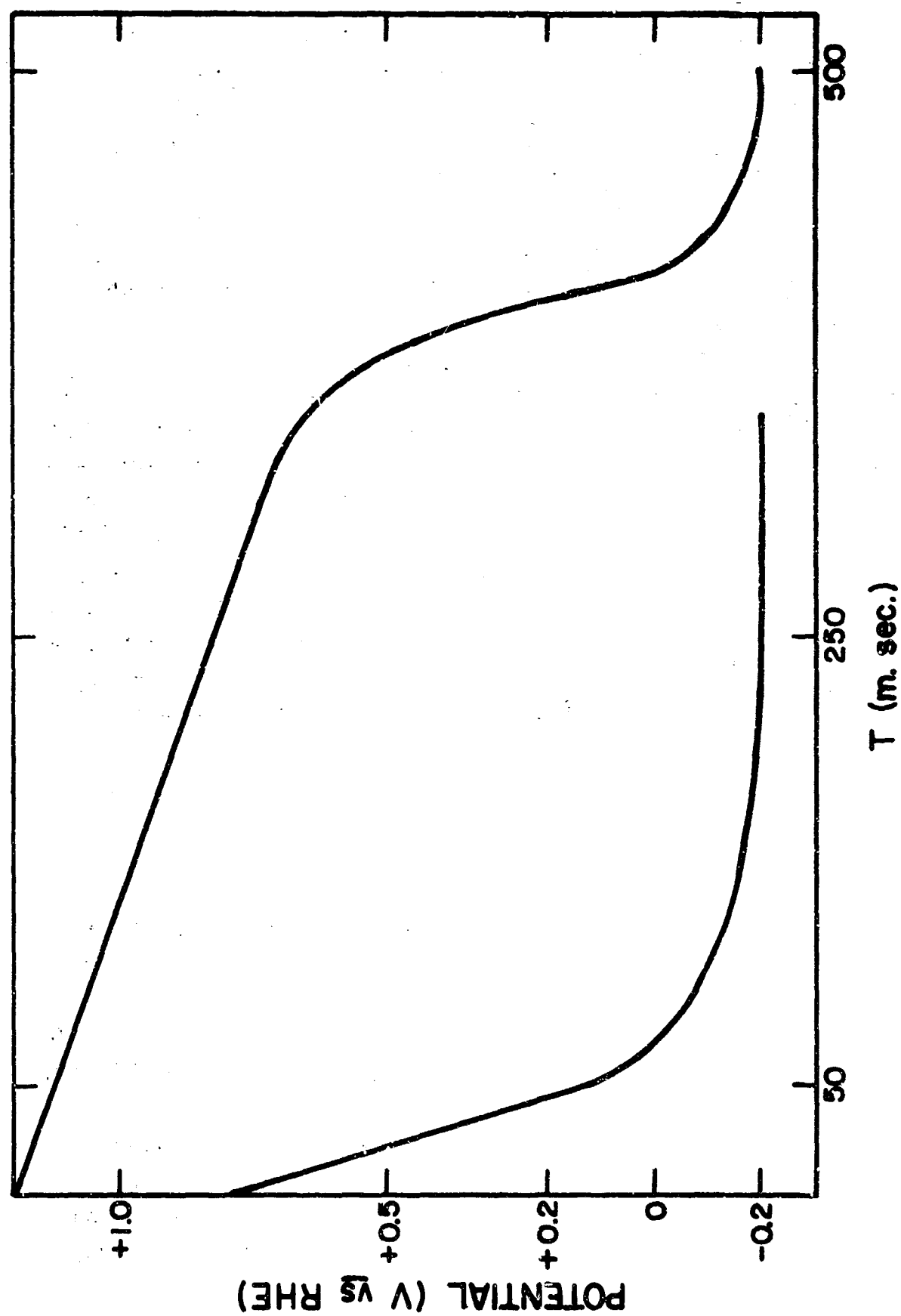
Fig. 38. Cathodic chronopotentiograms (200 mA/cm^2) of 80 Zn - 20 Ni in 6N KOH from 0. 8 and 1.2 v.

Fig. 39 Activation of passive 78 Zn - 22 Ni as a function of time at 0.0 v in 6N KOH. Before each point, the passive electrode was polarized for 60 sec at the indicated potential.
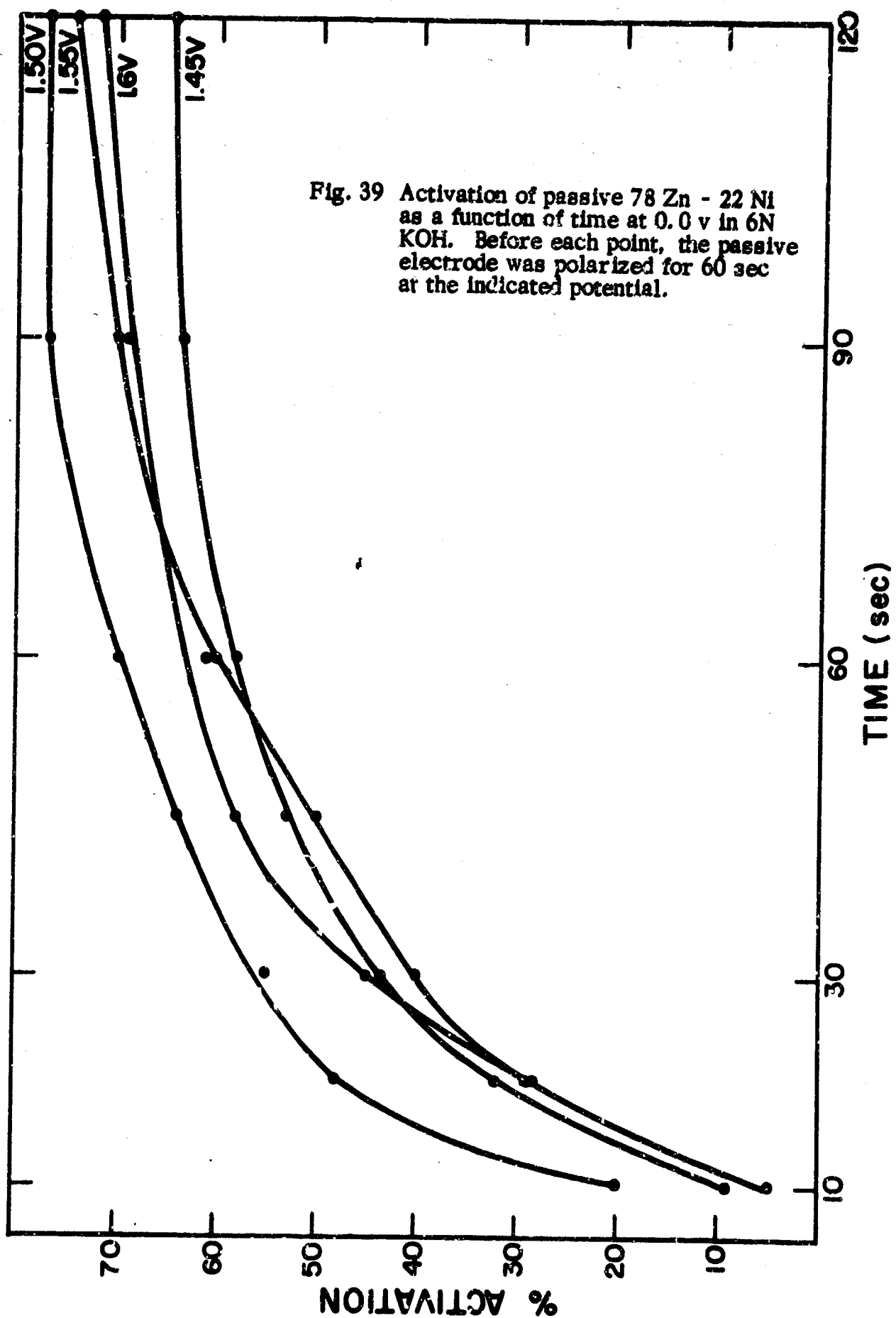
to the current obtained at 0.0 v for a fresh surface of the same electrode. The ratio can be considered as a percent activation and is, in fact, so denoted on the figure.

The results show that anodic pretreatment of a passive electrode leads to activation (~70%) in times between 20 and 60 sec. There are some differences between the lowest and the highest potentials used, but these are relatively minor. Figure 40 shows the effect of time at the second potential, in this case 1.6 v, on the ease of activation. The potential sequence was the same as in Fig. 38, but now the electrode was left at the more positive potential for times varying between 5 and 60 sec. The figure shows that the ease of passivation increases the longer the electrode is pre-polarized at 1.6 v. Under the best conditions, 60 sec at 1.6 v, 75% of activation is achieved in a total time of 90 sec (60 sec at 1.6 v and 30 sec at 0.0v).

The reproducibility of these results is illustrated in Fig. 41 which shows a duplicate series of runs for 20 and 30 sec at 1.6 v. In general, active currents were reproducible to about 10%.

The long term behavior of 80 Zn - 20 Ni alloys is shown in Fig. 42. The electrode was polarized in steps using a potential of 0.6 v and kept there over the next 70 hrs. The current in 6N KOH decayed from 1.8 ma/cm^2 at the end of 5 min. to 0.1 ma/cm^2 by the end of about 10 hrs. and essentially remained at this value thereafter. This is to be contrasted with the behavior of the Zn-Co alloys, which was described above.

The same alloy was studied in 1N KOH and the results are also shown in Fig. 3 . The current at 0.6 v at the end of 5 min. was 0.3 ma/cm^2 and then decayed to about 0.003 ma/cm^2 in approximately the same time and remained in the range of .001 to .003 over the next 50 hrs.

2.   Alloys in the β_1-phase

Homogeneous Zn-Ni alloys in the β_1-phase were prepared similarly to the Zn-Co alloys. The composition is 45% Ni - 55% Zn.
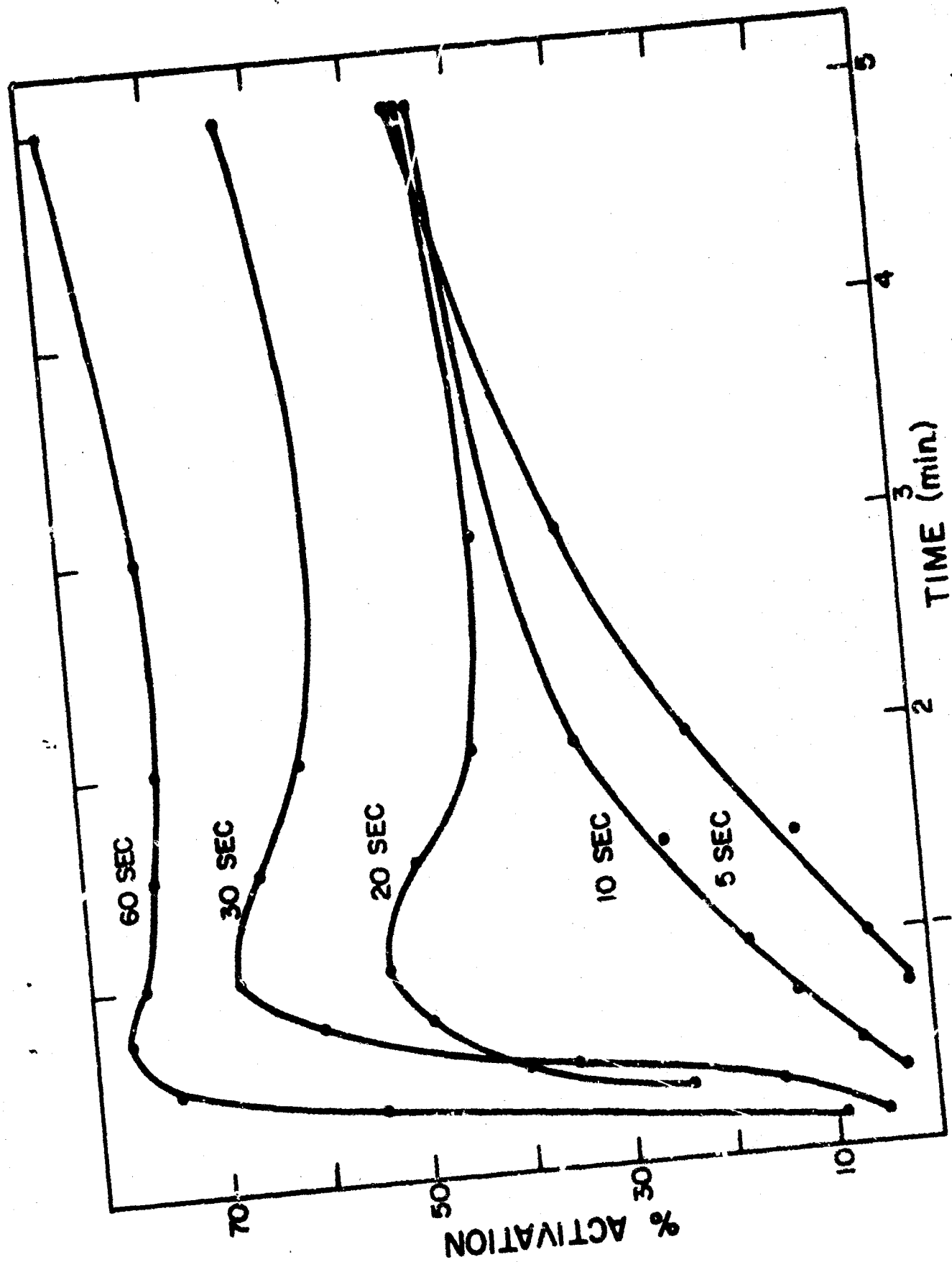
Fig. 40. Activation of 78 Zn - 22 Ni as a function of time at 0.0v in 6N KOH. Before each point, the passive electrode was polarized to 1.6v for a time indicated on the curves.

- 79 -
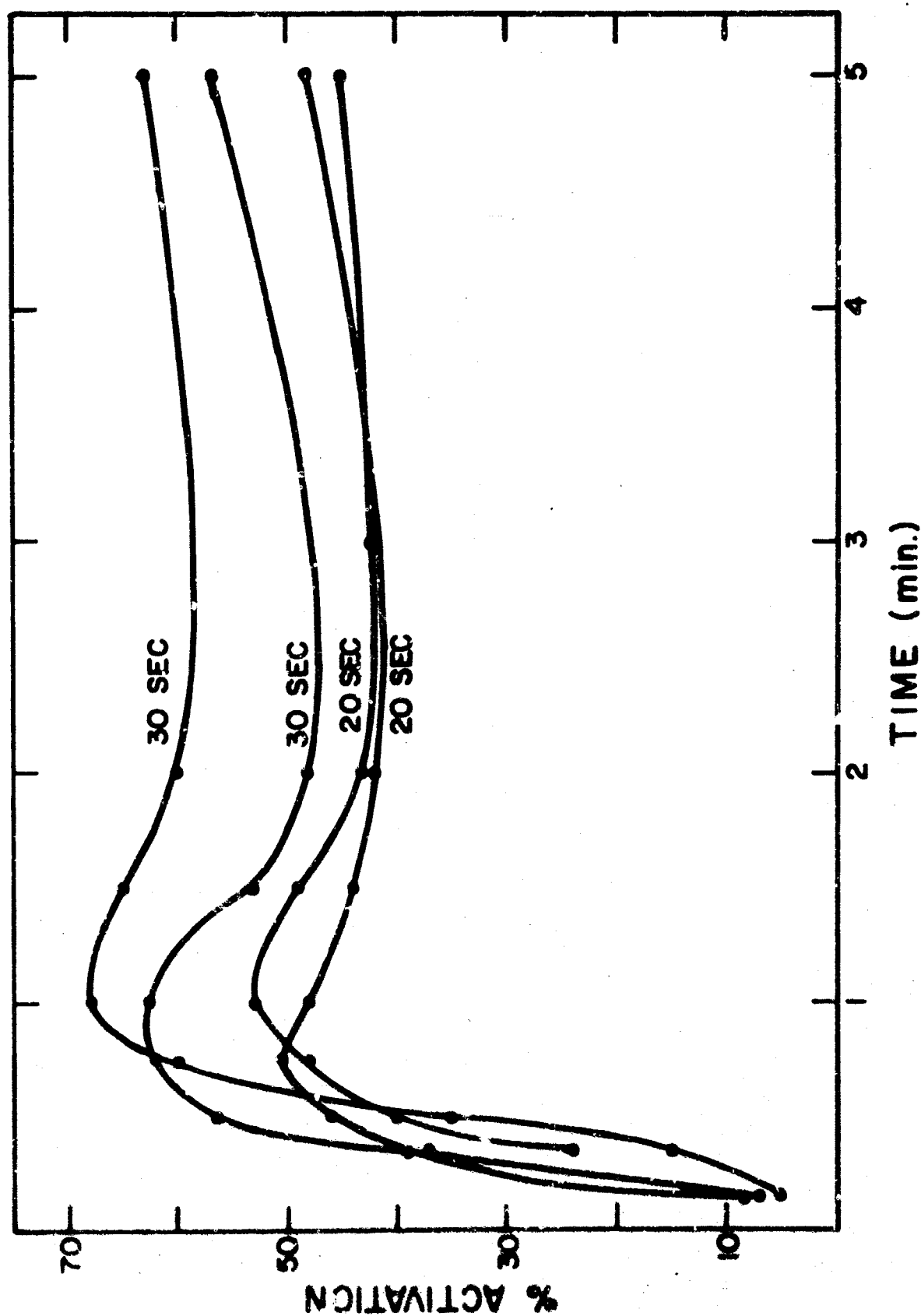
Fig. 41. Activation of 78 Zn - 22 Ni as a function of time at 0.0 v. Conditions as in Fig. 40
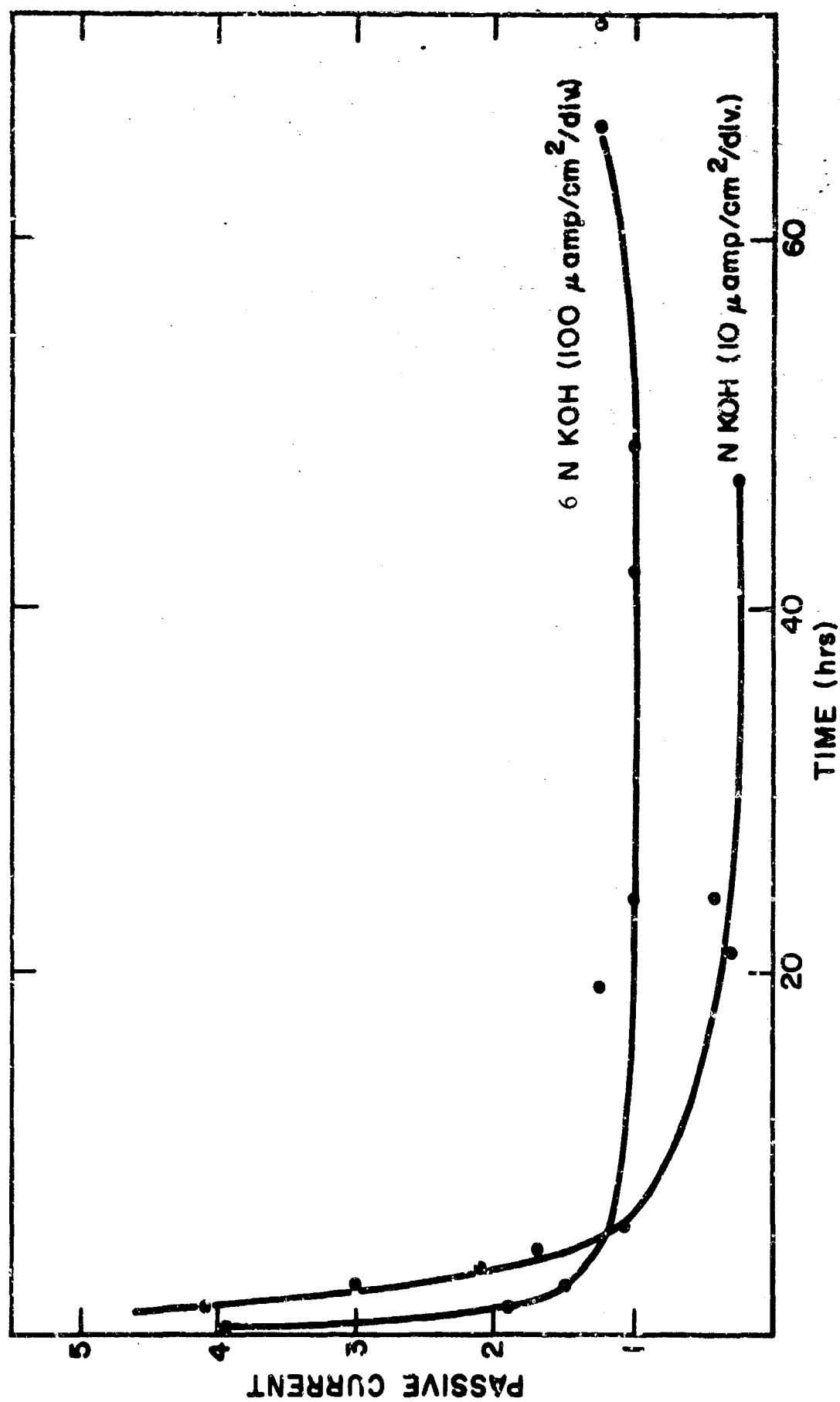
Fig. 42. Passive Current at 0.6 v for 20% Ni-Zn in 1 N and 6 N KOH 30°C, unstirred

An electrode made from this alloy was passive or very nearly passive even at very low potentials. The electrode generally tended to show cathodic currents even at 0.0 volts vs R.H.E. and the active dissolution region was non-existent. Cathodic polarization had a negligible effect. It was apparent that an alloy with such a high percentage of Ni is not useful as a battery electrode.

3. Summary of Characteristics of Zn Alloys

The results with zinc and zinc alloys in N and 6N KOH are summarized in Table III. Alloying, in general, shifts the dissolution curve in the active region to more positive potentials; the critical passivation potential is also displaced to more positive values. The passive current is decreased by factors up to 100. Long-term currents show even greater differences since the passive current on zinc is not time-dependent, while for the most promising alloys, it decays with time.

The passive currents can be modified substantially by additions of larger quantities of either Co, Zn or Ni. As expected, the active dissolution characteristics are also modified towards smaller dissolution currents at any given potential in the active region. The critical potential is also shifted to more positive values, but this effect is relatively small.

Table III

Critical Potentials and Currents and Passive Currents of Zn Alloys

$(30.0^{\circ}C)$

Electrode	Critical Potential	Critical Current	Passive Current (at 0.6 to 0.8 v)
Zn (1N KOH)	-0.1 v	32 ma/cm^2	7 ma/cm^2
Zn (6N KOH)	-0.2 v	275 "	80 "
80 Zn-20 Ni (1N)	+0.1 v	6 ma/cm^2	0.07 ma/cm^2
80 ZN-20 Ni (6N)	+0.1 v	50 "	0.3 "
78 Zn-22 Co (1N)	0.0 v	7.5 ma/cm^2	0.1 ma/cm^2
78 ZN-22 Co (6N)	0.0 v	110 "	2.8 "
89 Zn-11 Co (1N)	+0.1 v	15 ma/cm^2	1.0 ma/cm^2
89 Zn-11 Co (6N)	0.0	240 "	18 "
90 Zn-10 Fe (6N)	0.0	45 ma/cm^2	20 ma/cm^2
83 Zn-17 Mn (1N)	<-0.2	~ 3 ma/cm^2	2 ma/cm^2

Note: Values given for current are generally at the end of 5 min.

VIII. MIXED ELECTROLYTES

The anodic dissolution curves of the most promising alloys (namely 82 Zn - 18 Co and 80 Zn - 20 Ni) were obtained in N KOH containing neutral salts. The purpose of this study was to explore the possible electrolyte compositions which had sufficient conductivity for batteries but at the same time gave more favorable passive currents for the battery anode. We explored systems containing sulfate, perchlorate, chloride, and fluoride salts.

a) 82 Zn - 18 Co Alloys

The anodic dissolution curve of the 82 Zn - 18 Co alloy in N KOH and 0.4 M K_2SO_4 ($\sim$ a saturated solution) is shown in Fig. 43. If we compare this with the results for the same alloy in N KOH solution (see Fig. 31) we find small changes in the critical current and passive current, while the critical potential remains essentially unchanged at 0.0 v. The critical current decreases from 7.5 to 5.5 mA/cm^2, while the passive current increases from 0.1 to 0.15 mA/cm^2.

Figure 44, gives similar results for this alloy in a solution N in KOH and KCl. Again, the critical potential and the critical current are essentially unchanged. The passive current is also of the same order as in KOH alone. However, the passive current in chloride solutions increases with time, while in KOH, it decays with time. For example, at 0.6 v the current in N KOH and N KCl increases from 0.045 mA/cm^2 to 0.12 mA/cm^2 in 15 hrs. The opposite behavior was observed in KOH. (See arrow in Fig. 31). The increase of the passive current with time may be due to the well-known tendency of Cl ion to penetrate passive films, and, in some cases to produce pits.

Data on 82 Zn - 18 Co in M $NaClO_4$ - N NaOH solutions are shown in Fig. 45. Solutions containing sodium rather than potassium ion were used because the potassium salt of the perchlorate anion is not sufficiently soluble.

Similar data for this alloy in M KF - N KOH solutions are shown in Fig. 46. These data, together with data previously reported for chloride and sulfate solutions are summarized in Table IV, in terms of the critical current and potential and the passive current (at a fixed potential of 0.6 v).
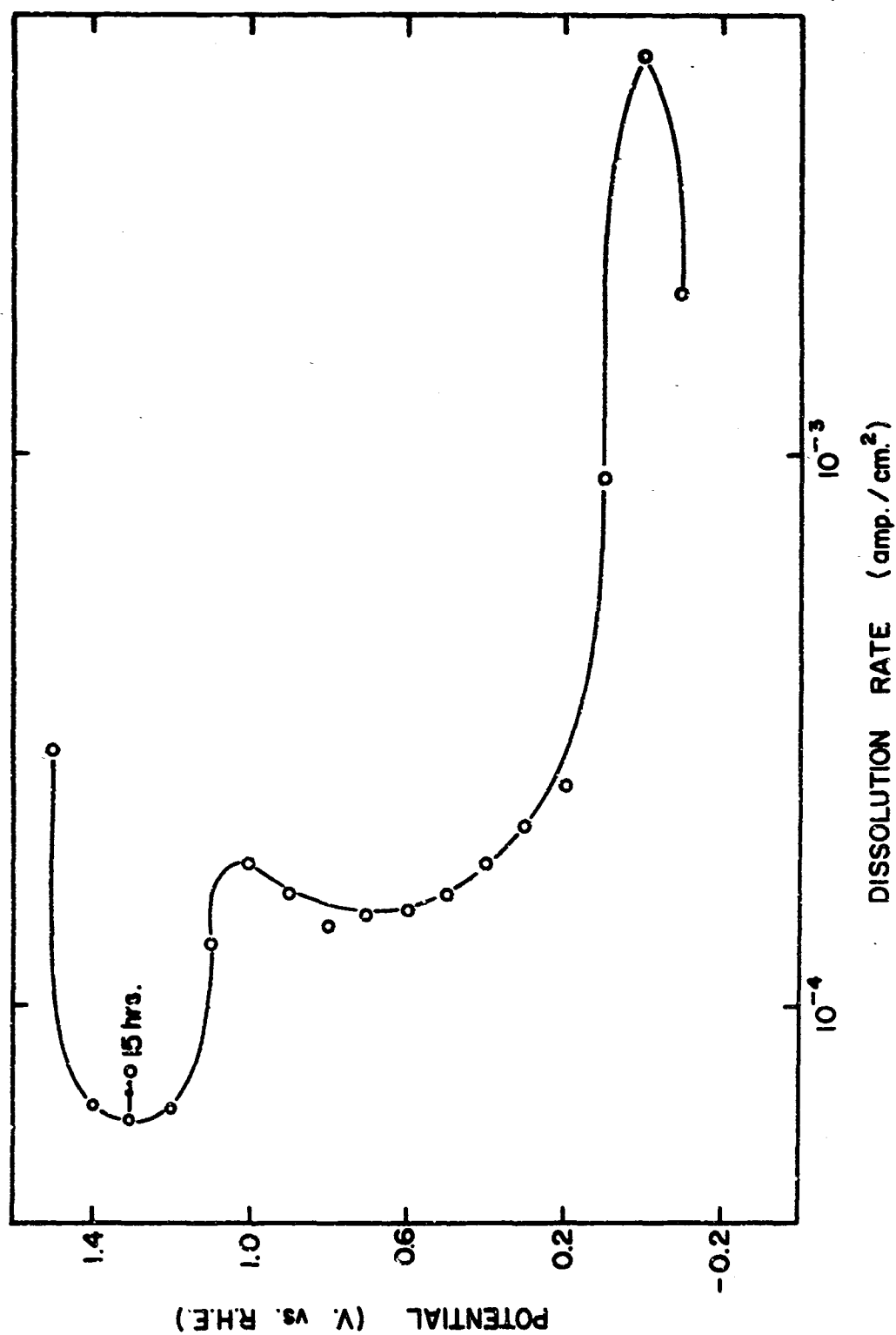
Fig. 43   Anodic Dissolution of 82 Zn - 18 Co in N KOH and 0. 4M K_2SO_4 (satd), unstirred

Fig. 44. Anodic Dissolution of 82 Zn - 18 Co in N KOH and M KCl, unstirred, 30°C.

• ALL 10 MIN. POINTS
  FRESH SOLUTION

DISSOLUTION RATE (amp./cm².)

POTENTIAL (V. vs. R.H.E.)

15 hrs.

20 min.
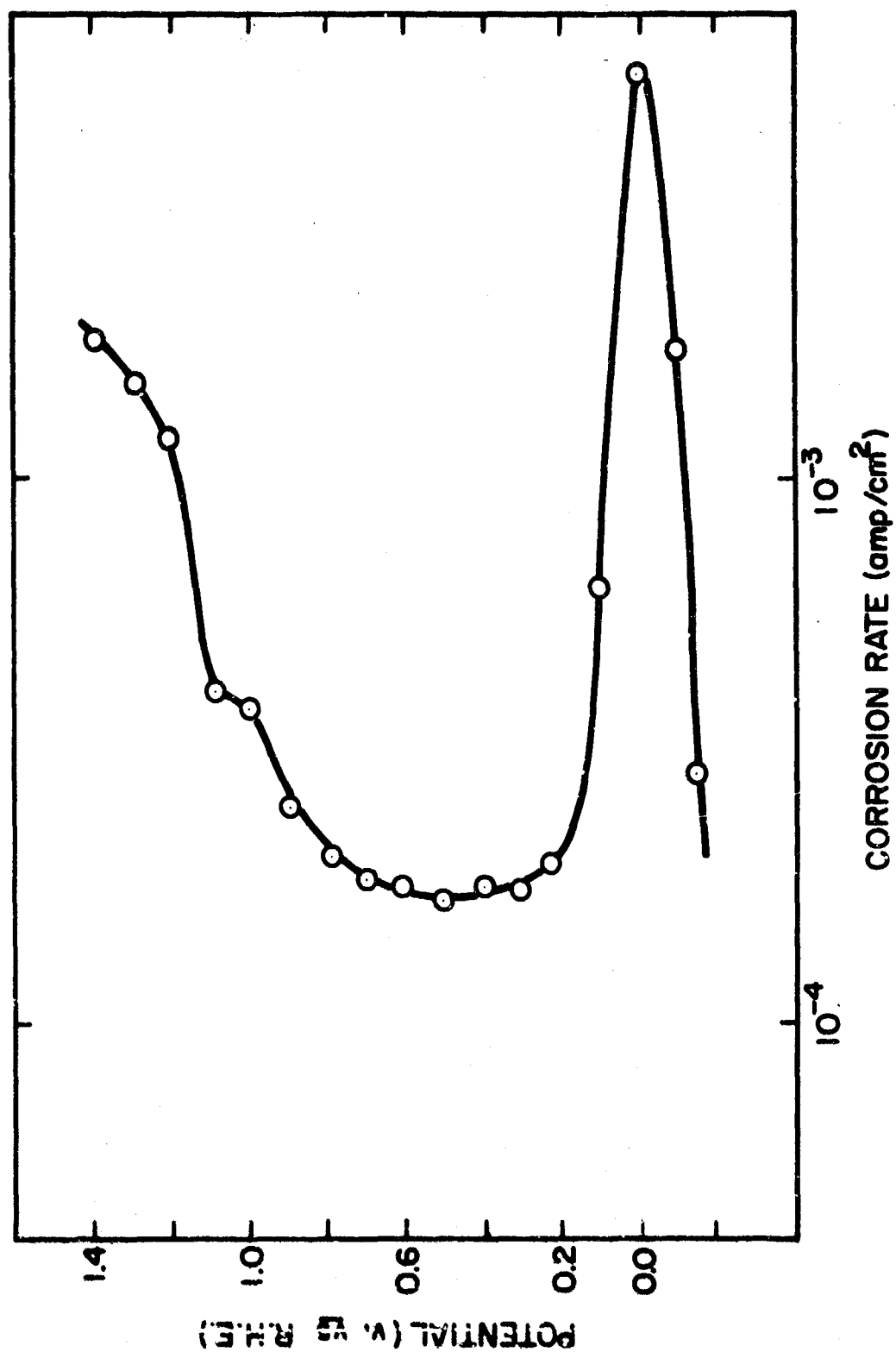
Fig. 45. Anodic Dissolution of 82 Zn - 18 Co in N NaOH and M NaClO$_4$, 30°C unstirred.

CORROSION RATE (amp./cm^2)

Fig. 46. Anodic Dissolution of 82 Zn - 18 Co in N KOH - M KF, 30°C, unstirred

POTENTIAL (v. vs R.H.E.)

10^{-3}

Table IV (a)

Dissolution Characteristics of 82 Zn - 18 Co at 30° C

Solution	i_{crit}(amp/cm^2)	E_{crit}(v vs R.H.E)	i_{pass}(amp/cm^2) at E = 0.80 v
N KOH[1]	7.8×10^{-3}	0.0	1.0×10^{-4}
N KOH + 0.4 K$_2$SO$_4$(sat)[2]	5.2×10^{-3}	0.0	1.5×10^{-4}
N KOH + M KCl[2]	5.7×10^{-3}	0.0	1.4×10^{-4}
N NaOH + M NaClO$_4$[2]	5.5×10^{-3}	0.0	1.7×10^{-4}
N KOH + M KF[2]	6.6×10^{-3}	0.0	3.3×10^{-4}

(1) These data were obtained with an alloy 77.8 Zn - 21.6 Co
The higher the Co concentration, the smaller the expected i_{pass}.

(2) These data were obtained with an alloy 82.3 Zn - 17.3 Co

Table IV (b)

Activation Characteristics of 82 Zn-18 Co at 30°C [1]

Solution	i_{crit}(amp/cm^2)	% Activation
N KOH + 0.4K$_2$SO$_4$ (sat)	2.6×10^{-3}	50
N KOH + M KCl	2.5×10^{-3}	44
N NaOH + M Na ClO$_4$	1.65×10^{-3}	30
N KOH + M KF	4.2×10^{-3}	65

(1) Electrodes activation by 125 ma/cm^2 cathodic, galvanostatic pulse.

Activation Characteristics of 82 Zn - 18 Co in Mixed Electrolytes

Activation of passivated alloys in solutions containing inert salts was studied as in Sec. VII. As before, it was found that the cobalt alloys could be activated with greater ease than the nickel alloys. The activation behavior in salt solutions was generally similar to that in N KOH alone. The general behavior of Co alloys is illustrated in Table IV (b).

b) 80 Zn - 20 Ni Alloys

The behavior of 80 Zn - 20 Ni in solution containing sulfate (Fig. 47) and chloride (Fig. 48), is substantially the same as in N KOH alone. The passive potential remains unchanged at about + 0.1 v and the critical current at between 6 and 8 mA/cm^2. The passive current is also little affected, being generally about 0.1 mA/cm^2. It appears that the passive current may be somewhat higher in the solutions containing the inert salt that it is in KOH alone.

Potentiostatic curves run on the 80 Zn - 20 Ni M $NaClO_4$ - N NaOH and M KF - N KOH are shown in Figs. 49 and 50. These data, together with results for chloride and sulfate solutions are summarized in Table V.

Activation Data:

Activation of passivated alloys in solutions containing inert salts was studied as before (see Sec. VII).

Zn-Ni alloys did not activate well directly and it was necessary to follow the anodic - cathodic sequence described previously for KOH solutions alone. The results were essentially the same as in N KOH alone.

The long-term behavior of these alloys has not been studied in detail. Some data were obtained in N KOH + 0.4 M K_2SO_4 (sat) solutions. The passive current at 1.2 v in 15 hrs was 7.5×10^{-5} amp/cm^2 and the specimen, after activation by a cathodic pulse of 100 ma/cm^2, showed a critical current of 3.9 ma/cm^2, or 75% activation. It should be pointed out that 1.2 v falls within the region of secondary passivation, i.e., when a higher valence oxide is apparently formed.
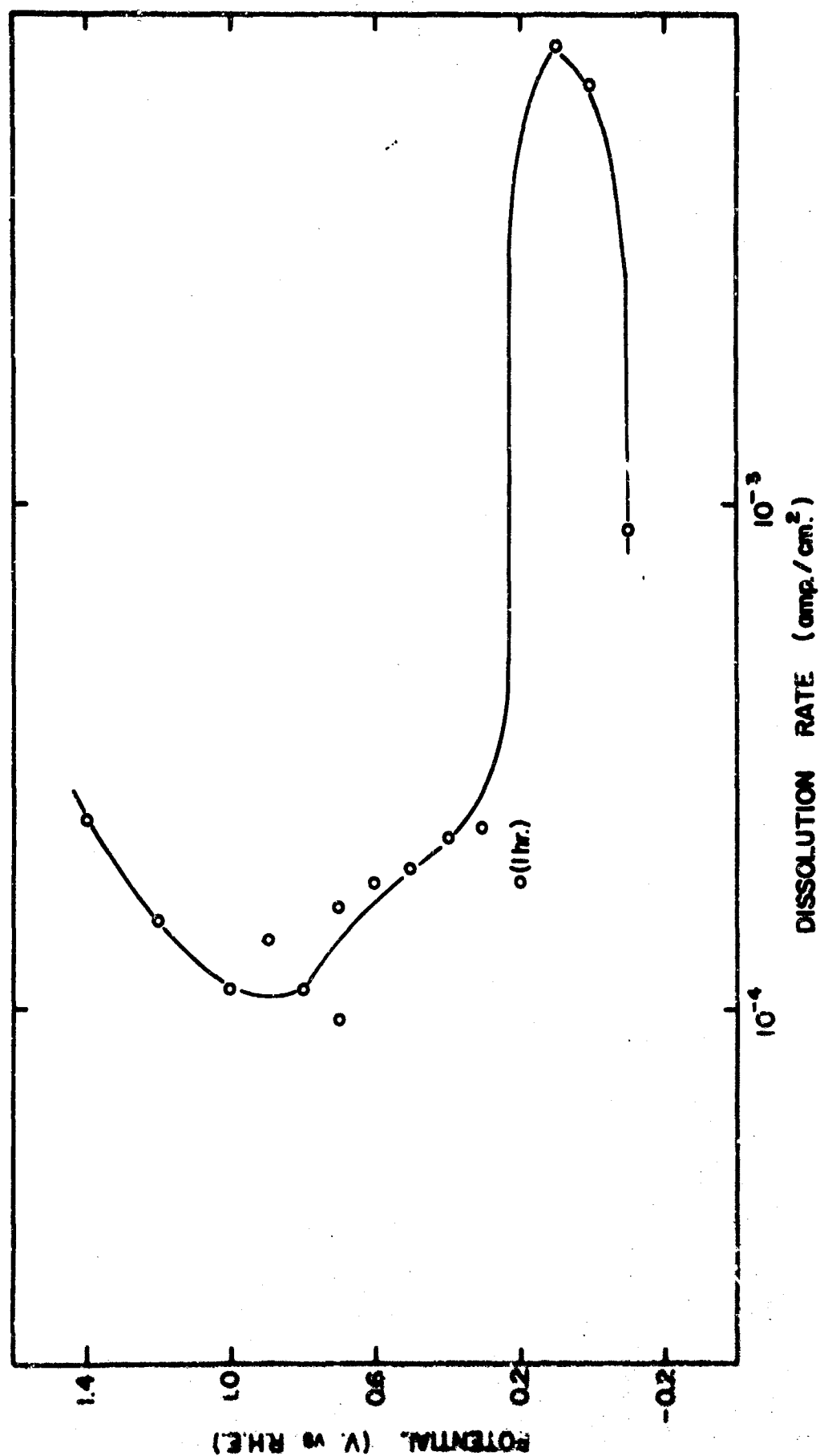
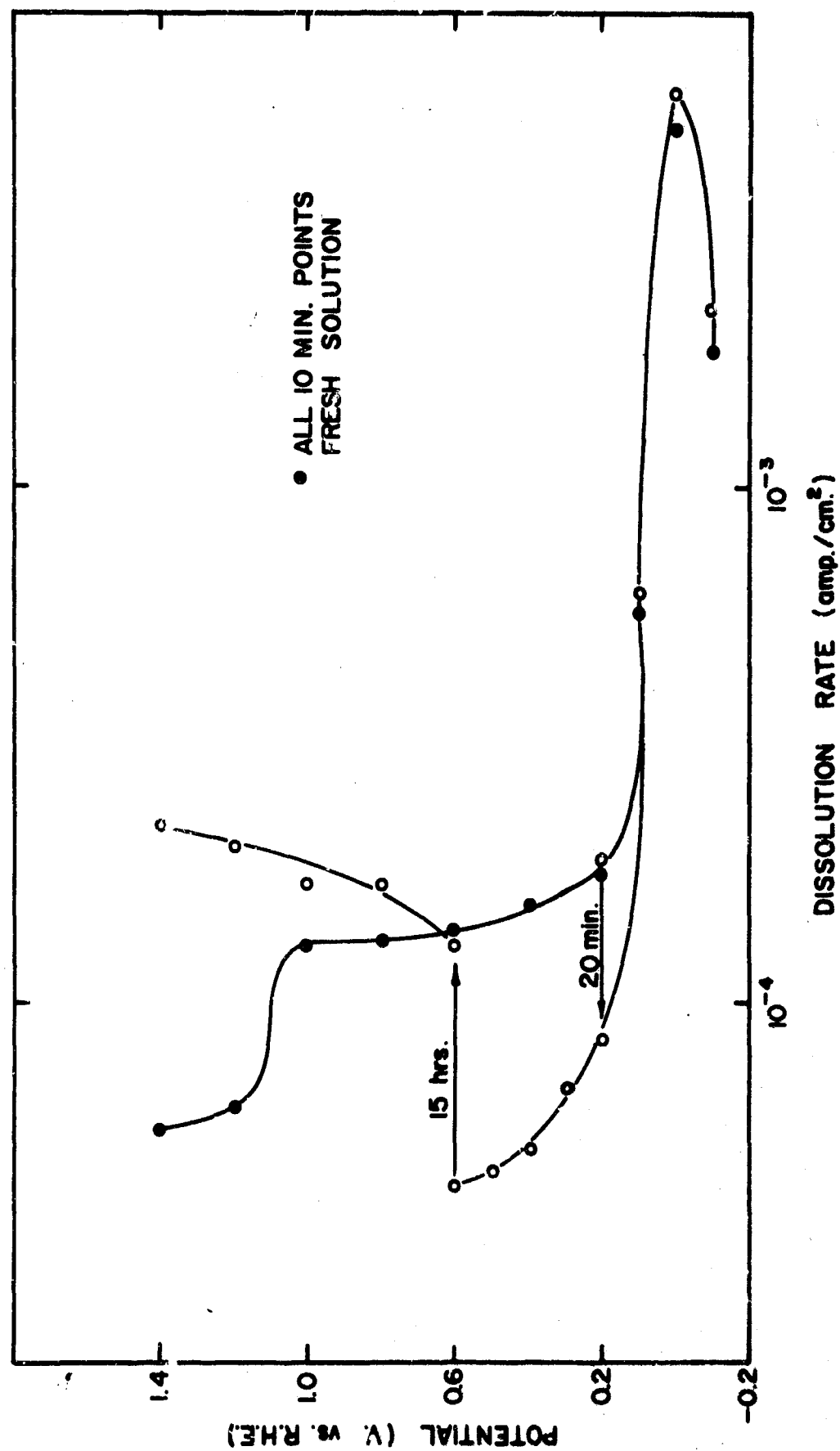Fig. 47. Anodic Dissolution of 80 Zn - 20 Ni in N KOH and 0. 4 M K_2SO_4 (sat'd), unstirred 30°C.
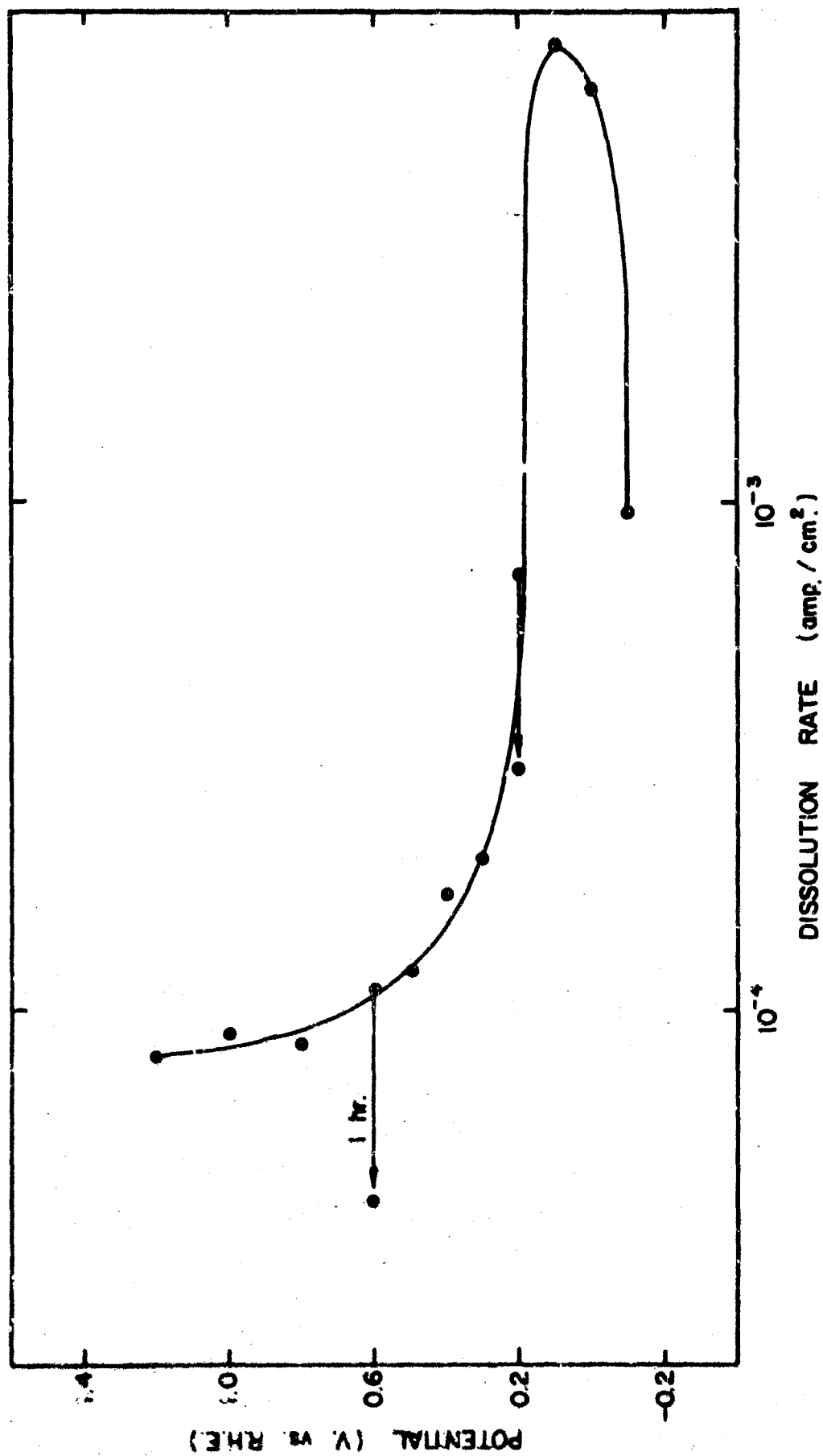
Fig 48. Anodic Dissolution of 80 Zn – 20 Ni in N KOH and M KCl, unstirred, 30°C

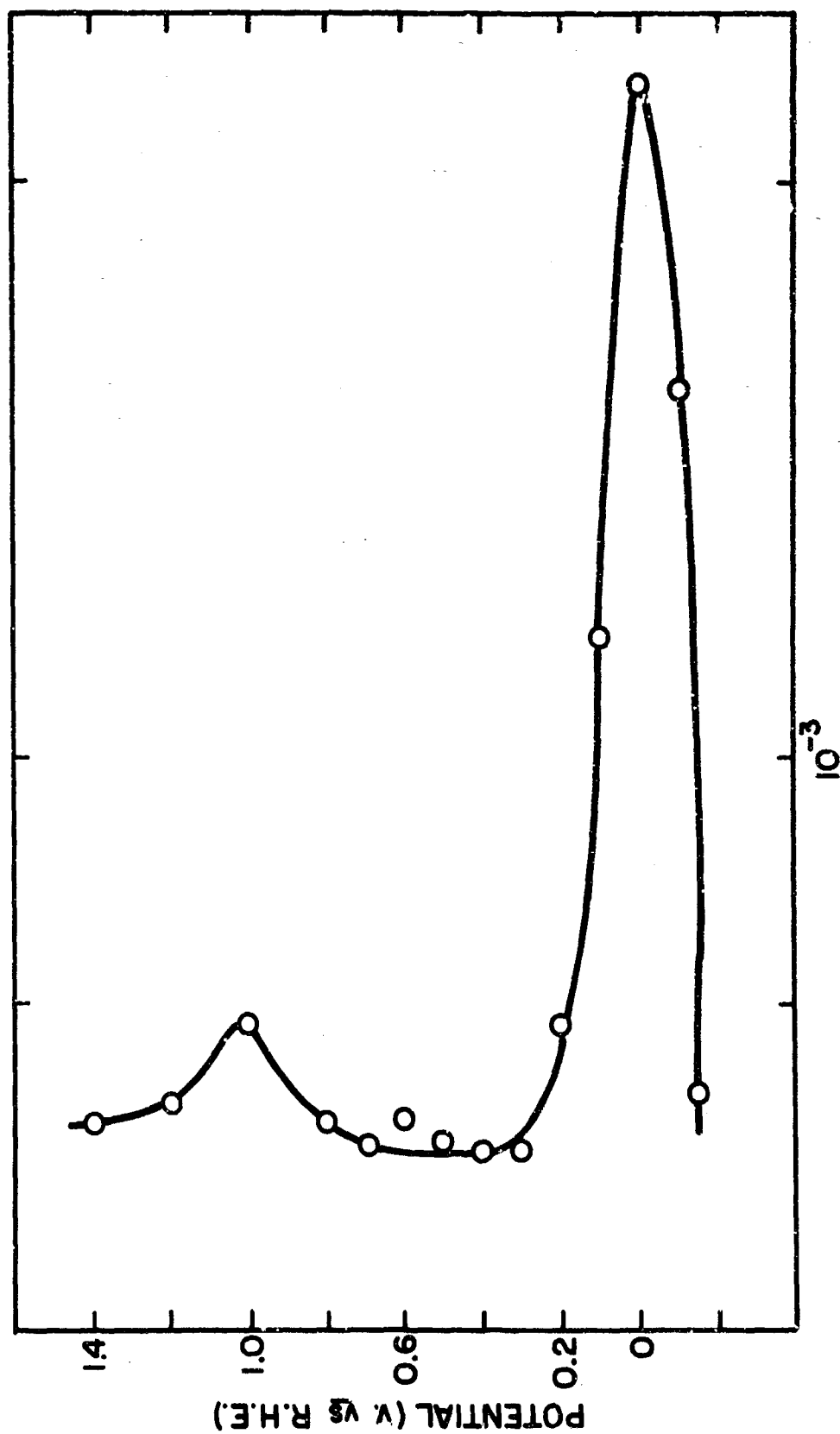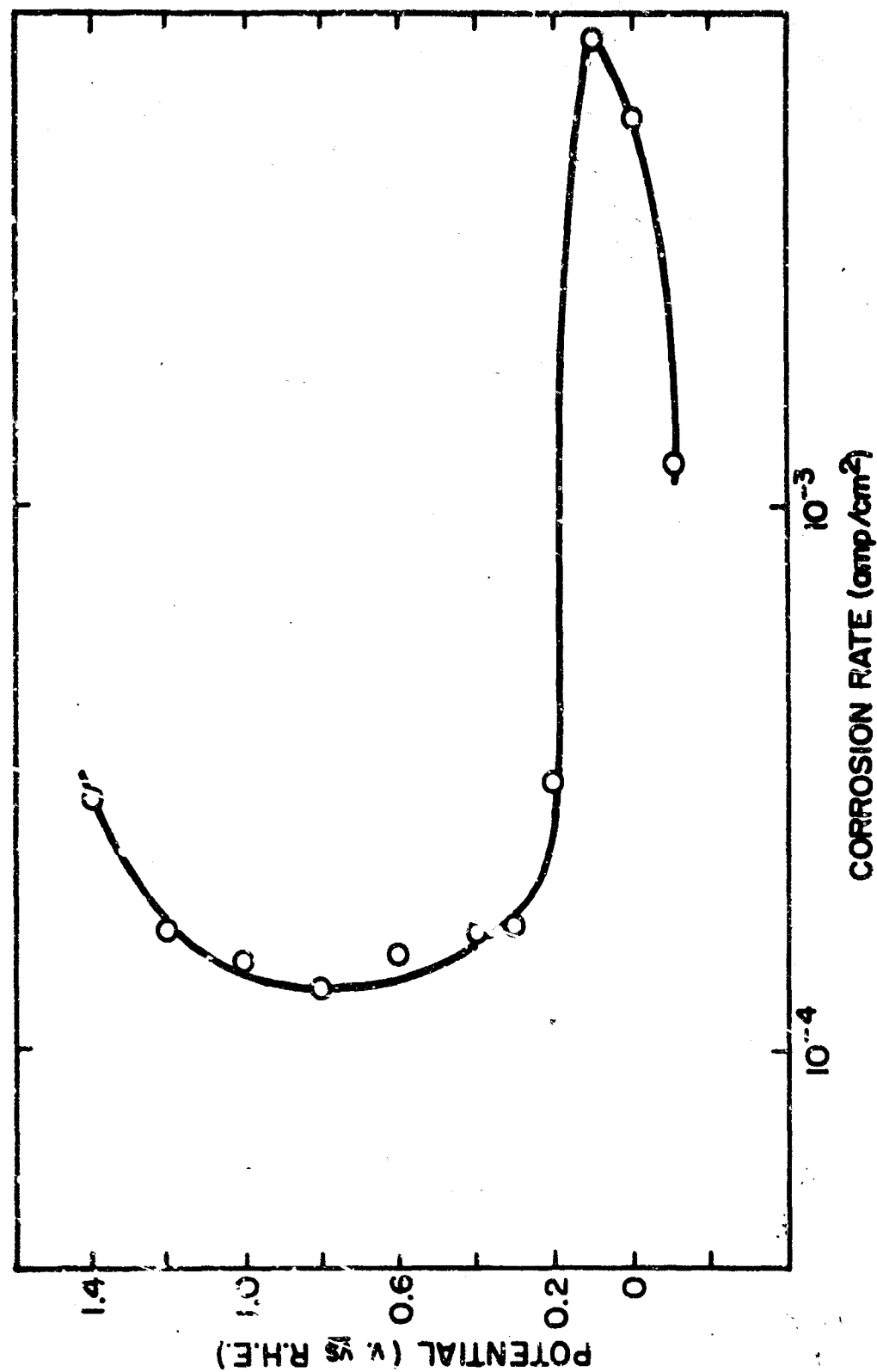Fig. 49. Anodic Dissolution of 80 Zn - 20 Ni in N NaOH, M NaClO$_4$, 30°C, unstirred.

- 93 -
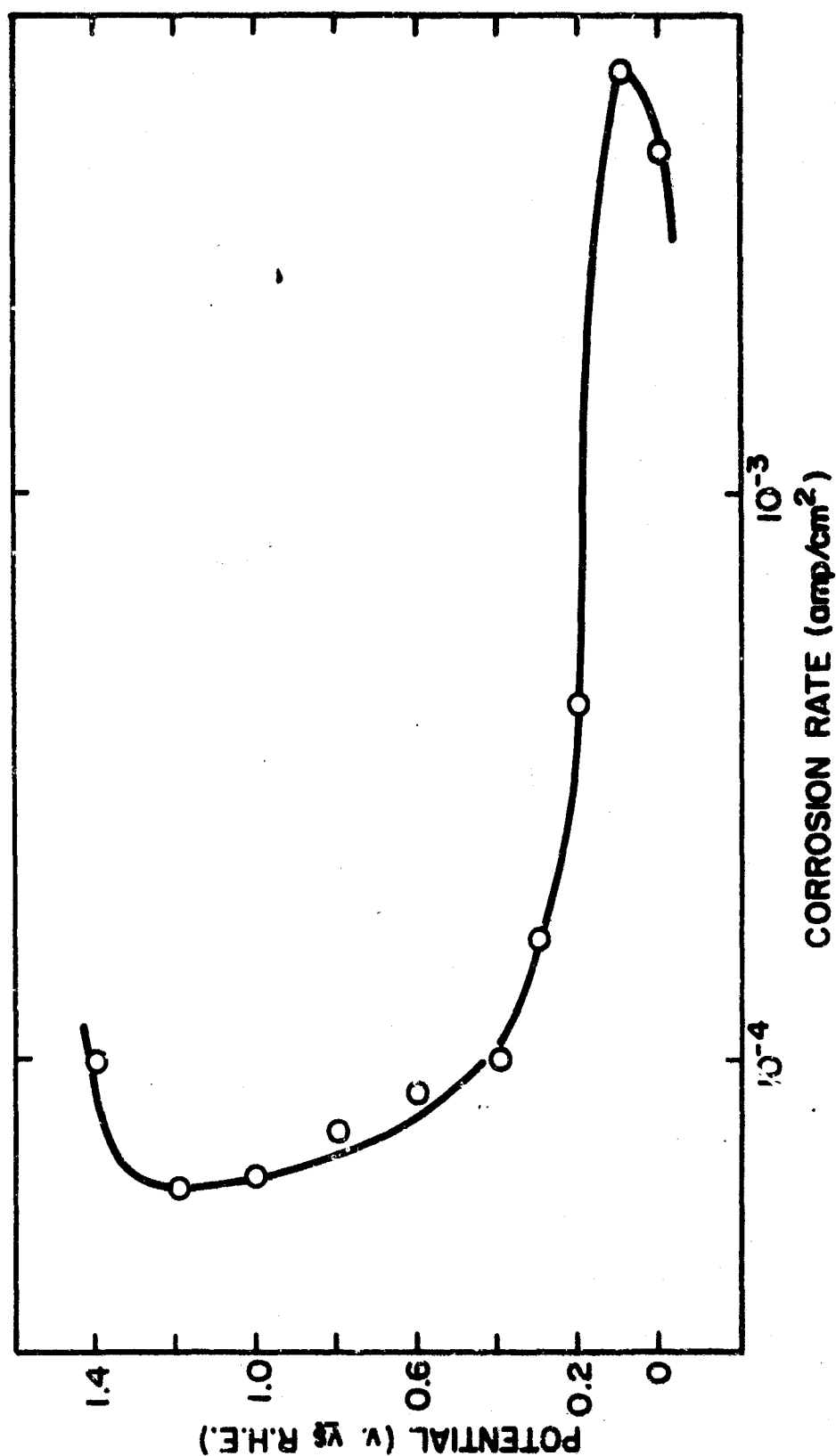
Fig. 50. Anodic Dissolution of 80 Zn - 20 Ni in N KOH and M KF, 30°C, unstirred.

Table V

Dissolution Characteristics of 80 Zn - 20 Ni at 30° C

Solution	i_{crit} (amp/cm^2)	E_{crit} (v $\underline{vs}$ R.H.E)	i_{pass} (amp/cm^2) at E = 0.8v
N KOH[1]	6.0×10^{-3}	0.10	6.8×10^{-5}
N KOH + 0.4 M K$_2$SO$_4$ (sat)	7.8×10^{-3}	0.10	1.1×10^{-4}
N KOH + M KCl	7.8×10^{-3}	0.10	9.0×10^{-5}
N NaOH + M NaClO$_4$	7.2×10^{-3}	0.10	1.3×10^{-4}
N KOH + M KF	5.6×10^{-3}	0.10	6.8×10^{-5}

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(1)   These data obtained with 79.2 Zn - 20.3 Ni
(2)   These data obtained with 81.9 Zn - 17.9 Ni

c) Cathodic Polarization Curves

Cathodic polarization curves were obtained in the mixed electrolytes. Examples of such curves are shown in Figs. 51 and 52. Data for the mixed electrolytes are summarized in Table VI. The Ni alloys are generally better hydrogen electrodes than the Co alloys. The Tafel slope is essentially the same for all solutions and both alloys suggesting the same mechanism for the hydrogen evolution reaction on all electrodes.

Conclusions

A N KOH electrolyte can be modified substantially by addition of inert salts without major changes in either the anodic or cathodic properties of 82 Zn - 20 Ni alloys or of their activation properties.
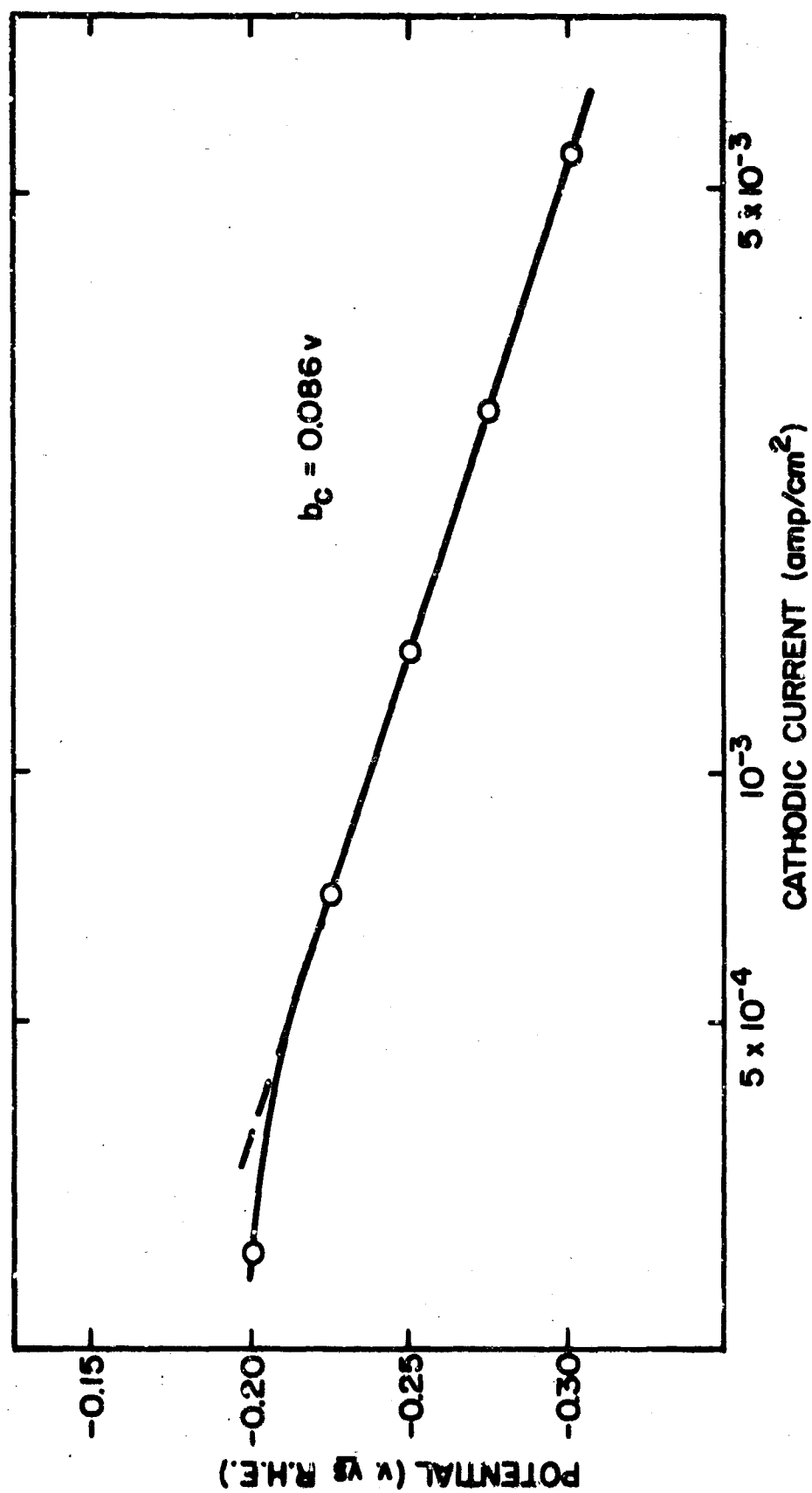
Fig. 51. Cathodic Polarization Curve on 82 Zn - 18 Co in N NaOH - M NaClO$_4$, 30°C
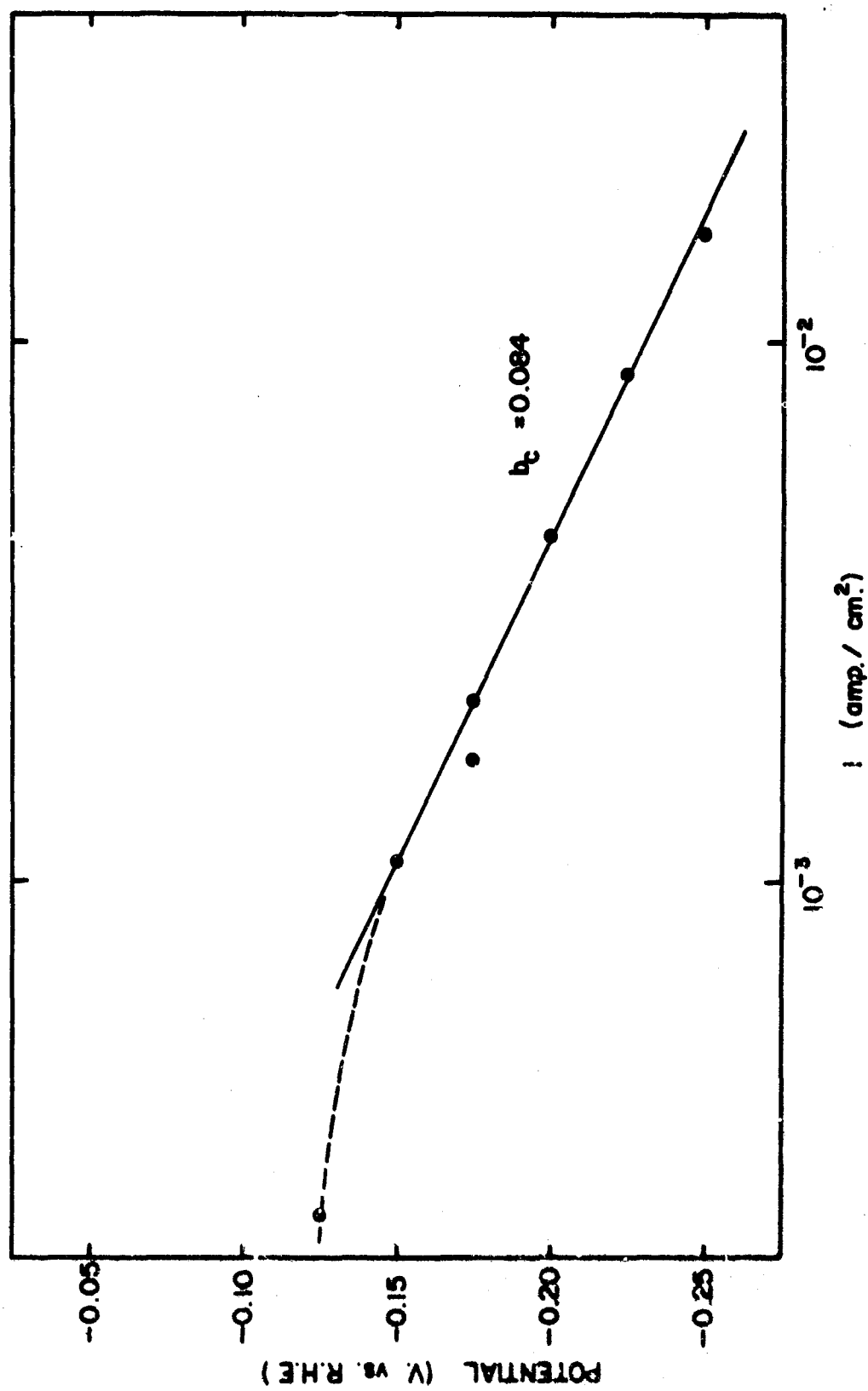
Fig. 52. Cathodic polarization curve for 80 Zn - 20 Ni in N KOH and M KCl at 30°C

Table VI

Cathodic Polarization Curves of 82 Zn-18 Co and 80 Zn-20 Ni in Mixed Electrolytes

(All runs made at 30°C prior to passivation)

82 Zn - 18 Co

Solution	Tafel Slope (v)	Current (amp/cm^2) at - 0.2 v vs R.H.E.
N KOH[1]	0.089	1.05×10^{-3}
N KOH + 0.4 M K$_2$SO$_4$(sat)[2]	0.083	0.78×10^{-3}
N KOH + M KCl[2]	0.078	1.20×10^{-3}
N NaOH + M NaClO$_4$[2]	0.086	0.36×10^{-3}
N KOH + M KF[2]	0.095	0.75×10^{-3}

80 Zn - 20 Ni[3]

Solution	Tafel Slope (v)	Current (amp/cm^2) at - 0.2 v vs R.H.E.
N KOH + 0.4 M K$_2$SO$_4$(sat)	0.085	2.4×10^{-3}
N KOH + KCl	0.084	4.4×10^{-3}
N NaOH + M NaClO$_4$	0.084	1.3×10^{-3}
N KOH + M KF	0.080	8.0×10^{-3}

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(1) Alloy 77.8 Zn - 21.6
(2) Alloy 82.3 Zn - 17.3 Co
(3) Alloy 81.9 Zn - 17.9 Ni

IX. COMPARISON OF PRIMARY, PASSIVE BATTERIES TO GAS ACTIVATED BATTERIES

The main advantage of a primary battery operated in the passive mode over conventional reserve batteries is the possible saving in weight and volume because of the elimination of separate storage of electrolyte. In this section we attempt to compare primary batteries activated by a gas generator fired system with passive batteries. Since these batteries are in an early stage of development, it is difficult to arrive at anything more than semi-quantitative estimates.

We consider two types of reserve batteries: Silver-Zinc activated by a gas generator and Magnesium-Dinitrobenzene activated by ammonia vapor.

Although there are several reports in the literature on activation systems, detailed data on comparative volumes and weights are lacking since these are apparently not standardized. In Table VII we have collected data available to us; from these we made an attempt to estimate the contribution of the activator system to the total weight and volume. It appears that the activator amounts to about 25 to 30% of the battery weight and to about 80 to 90% of the battery volume.

Batteries employing a Mg/DNB couple (or m-DNB), have stored electrolyte or ammonia in a separate compartment. They are activated by firing pyrochemicals which rupture the liquid container and introduce ammonia into the plates. Engineering data are not generally available. However, we have compiled in Table VIII what are the goals of current development efforts; present systems approximate, but do not quite achieve, the performances indicated. It should be noted that the systems described in Table VIII were designed to minimize volume rather than weight. The contributions of the various components to the total weight are not available exactly, but the following approximate values have been obtained for the FC-2 battery (see Table VIII). The battery section, i. e. active materials, electrode structures, and separators, accounts for about 10% of the total weight. The rest of the weight is electrolyte and activator system. The weight is approximately distributed as follows:

Table VII

Gas Generator Fired Activation Systems

Battery	Battery Weight	Activator Weight	Battery Volume	Activator Volume	Watt hrs/lb	Watt hrs/in^3
Ag-Zn Model[1]	36.25 lb	11.00 lb	516.0 in^3	445.0 in^3	32.5	1.60

Battery	Volts/Amp	Total Weight	Total Volume	Watt hrs/lb	Watt hrs/in^2
34 x PA-50[2]	47/500	70.0	1460	39.0	1.87

(1) Representative Battery of the Current State-of-the-Art
(2) P. L. Howard, 12th Ann. Power Sources Conf. 1958, p. 41.

Table VIII

Ammonia Reserve Batteries

Battery	Voltage (v)/ Current (ma)	Time (hrs)	Size (in^3)/ Weight (lb)	Wt-hrs/lb	Activation Time
NOLC	28/1000	0.08	6.1/0.618	10.0	1 sec
Eglin AFB	9.0/15	36.	10.3/1.30	3.7	0.3±0.1 sec
Picatinny	24/50	50.	98./9.05	5.5	3 sec
BuWeps	28/5000	0.1	12.2/1.1	12.7	2 sec
Picatinny	16/35	0.017	0.91/0.11	.085	0.025 sec

(4) W. C. Spindler "Review of Recently Developed Liquid Ammonia Batteries", AD 624768, (1965)

Total Weight	285 g
Battery	30 g
Electrolyte	10 g
Activator	15 g
Ammonia Container	120 g
End Plates	80 g
Case	50 g

We estimate that about 70 to 75% of the total weight and about 20% of the volume is associated with separate storage of the electrolyte.

We have, therefore, two extreme conditions: In one case the weight contribution is low (~25%) but the volume contribution high (~80%); in the other, the additional volume is low (~20%) but the added weight is high (~75%).

In order to estimate the minimum characteristics of a primary battery operated in the passive mode which would make it comparable to the above systems, we assume that the battery will be operated at 100 ma/cm^2 (about 600 ma/in^2) for 5 minutes. We also assume that the active material accounts for 50% of the weight of a battery (minus activator weight).

If the corrosion rate in the passive state is 1×10^{-6} amp/cm^2, there is a loss of about 30 coul/cm^2 per year. This requires an increase in active material, to make up for this loss, by a factor of 2. In view of the weight ratios estimated above, this increase in active material is equal to the saving in weight produced by elimination of a gas generator type of activator, provided all other factors remain the same. It is apparent, therefore, that a minimum acceptable corrosion rate is 1 μa/cm^2 (and that a desirable rate is 0.1 μa/cm^2). At this level, the weights are equal but there will be a substantial saving in volume. If we assume that the volume of the active material is also about 50% of the battery (less activator), we find a volume saving of about 50%.

The best value achieved in the current program (5-10 μa/cm^2) was higher than the minimum rate of 1 μa/cm^2 calculated above. Therefore, none of the anode-electrolyte combinations are suitable for application in the mode suggested. Although the above calculations are only approximate, they indicate that a corrosion rate of between 0.1 and 1.0 μa/cm^2 must first be achieved before any other optimization studies are attempted.

X. RECOMMENDATIONS FOR FUTURE WORK

One of the main results of the current study was that electro-chemical passivation of the zinc anode itself is possible but not satisfactory because the passive current is too high in both 1N and 6N KOH. This suggested alloying of zinc to modify its passivation characteristics. The corrosion resistance of a number of possible alloying constituents in alkaline solution was investigated. Co, Fe, Ni, Mg, Cu, Mn and Ti showed reasonably promising properties but the dissolution characteristics of zinc with Cu, Mg, Mn, and Fe showed that they were not, in fact, suitable for the present purpose.

The characteristics of the group VIII alloys, particularly those with Co and Ni, are promising. For example, the critical current for 81 Zn - 19 Co is $\sim$ 100 mA/cm^2 and the loss of potential due to alloying is only $\sim$ 0.15v. The ratio of passive to critical currents (= ratio of storage to discharge life) is still too low ($\sim$ 175 in 1 N KOH and $\sim$ 500 in 6 N KOH). The passive current in 1 N KOH (56 μA/cm^2) is scarcely acceptable but one may hope to improve this by further optimization. The results for Zn-Ni are even more promising since the duty/storage ratio is higher ($\sim$ 600 in 6 N KOH, $\sim$ 200 in 1 N KOH), and the storage life is longer (i_p is 32 μA/cm^2 in 1 N KOH). Activation of passivated Zn-Ni electrodes with cathodic pulses can be carried out after an anodic treatment. The anodic treatment probably injects higher valence ions and defects into the oxide lattice which facilitates reduction.

A second method of passivating a zinc anode in a silver/zinc battery was explored: mechanical passivation by plating of copper which was then removed with an anodic pulse. This mechanical passivation scheme was shown to be feasible for some of the electrodes. Suggestions have been made which show that such a protective layer could be applied to a pressed, porous zinc electrode.

Further lines of approach are:

1) Mechanical Passivation

The properties of some of the zinc anodes in alkaline solution with respect to dissolution should be investigated in the presence of

cupric ion. Plating (electrochemical or otherwise) of copper onto some of the zinc and subsequent dissolution of copper should be studied. Methods for incorporating copper into porous zinc electrodes and techniques for activating such electrodes should be examined. Other possible coatings for zinc and perhaps for magnesium should also be explored.

2) Electrochemical Passivation

The properties of Zn-Ni, Zn-Co, and Zn-Fe in alkaline salt solutions should be examined in mechanistic terms. In particular, the passivating films and their kinetics of formation and reduction should be characterized. An attempt should be made to generate a working hypothesis for suitably modifying the properties of passivating oxides by using ternary alloy systems. Electrolytes should be optimized for such systems.

Bibliography

The following references on passivation of Zn, Fe, Ni, Cd, and Mg in various solutions are arranged according to metal; in the case of alloys, the reference is given under the major constituent.

Zinc

"Processes taking place on the zinc electrode of an alkaline cell", Z. A. Iofa, S. Ya. Mirlina, and N. B. Moiseeva, Zhur. Priklad, Khim, 22, 983-94 (1949).

"Electrochemical potential and passivity of zinc in solutions of zinc nitrate and other nitrates", O. Scarpa, Ricerca sci. 19, 226-9 (1949).

"Potential-pH diagram of zinc and its application to the study of zinc corrosion", P. Delahay, M. Pourbaix, and P. Van Rysselberghe, J. Electrochem. Soc. 98, 101-5 (1951).

"Anodic layer of zinc", T. Inoue, M. Sato, and R. Ishii, J. Electrochem. Soc. Japan 22, 679-84 (1954).

"Influence of aging processes in the working of alkali zinc cells", V. N. Flerov, Trudy Chetvertogo Soveshchaniya Elektrokhim., Moscow 1956, 768-72 (Pub. 1959).

"Corrosion resistance of zinc alloys containing manganese and copper", S. Fujino, Nagoya Kogyo Gijutsu Shikensho Hokoku 5, 326-9 (1956).

"Anodic behavior of copper-zinc alloys in sodium cyanide solutions", I. W. Machu, A. M. Azzam, and G. M. Habashi, Werkstoffe u. Korrosion 8, 17-23 (1957).

"Film-forming processes on zinc anodes in sodium hydroxide solution", R. Landsberg and H. Bartlet, Z. Elektrochem. 61, 1162-8 (1957).

"Effect of some additives on the passivation of a zinc anode and on the performance of alkali zinc galvanic elements", V. N. Flerov, Zhur. Priklad. Khim. 30, 1326-30 (1957).

"The anodic oxidation of zinc and zinc-tin alloys at very low current density", S. E. S. El Wakkad, A. M. Shams El Din, and H. Kott, J. Electrochem. Soc. 105, 47-51 (1958).

"Corrosion of zinc by differential aeration", G. Bianchi, Corrosion, 14, 245t-248t (1958).

"Electrochemical behavior of zinc in alkaline solutions. I. Constant-current measurements.", I. Sanghi and W. F. K. Wynne-Jones, Proc. Indian Acad. Sci. 47A, 49-64 (1958).

"Corrosion studies. XXI. Passivation of zinc by chromium tert-butyl alcoholate in the gas phase", L. Certveny, Chem. listy 52, 2205-11 (1958).

"Mechanism of discharge of powdered zinc electrodes", V. N. Flerov, Zhur. Priklad. Khim. 32, 132-7 (1959).

"Corrosion and passive states of zinc, lead, and tin in the system water-oxygen-nitrogen-carbon dioxide", R. Uggla, Ann. Acad. Sci. Fennicae, Ser. A97, No. 2, 74 pp. (1959).

"Potentiostatic studies on zinc", I. Sanghi and M. Fleischmann, Electrochim. Acta 1, 161-76 (1959).

"Nucleus formation in supersaturated salt solution at the anodic passivation of cadmium, zinc, and lead", W. Lorenz, Z. physik. Chem. 20, 95-102 (1959).

"Study of passivating layers on zinc by the electronographic method", A. I. Levin, M. E. Prostakov, and G. D.Susloparov, Doklady Akad. Nauk. S.S.S.R. 129, 617-19 (1959).

"Increase in corrosion-resistant and decorative properties of zinc coatings by alloying with nickel", N. T. Kudryavtsev, K. M. Tyutina, and S. M. Firger, Trudy Moskov, Khim. -Tekhnol. Inst. im. D. I. Mendeleeva 1959, No. 26, 96-104.

"The kinetics of the process of coating formation on nickel and zinc anodes", R. Landsberg, Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg 1, No. 3, 205-6 (1958-59).

"Potential studies on passivity to corrosion induced by pretreatment processes. II. Comparative study of chromate treatment and chromate inhibition", K. S. Rajagopalan and K. Balakrishnan, J. Electrochem Soc. 106, 562-6 (1959).

"Anode passivation of zinc with a current of alternating polarity", L. K. Yuldasheva and F. F. Faizullin, Materialy Elektrokhim. Konf., Kazan, Sb. 1959, 65-6.

"Anode potentials of zinc in saturated zinc sulfate solution", K. Schwabe and F. Lohmann, Z. Physik. Chem. 215, 158-66 (1960).

"Anodic passivation of zinc in alkaline solutions", I. Sanghi and T. P. Radhakrishnan, Symposium on Electrodeposition Metal Finishing, Proc. Karaikudi, India 1957, 133-7 (Pub. 1960).

"Corrosion Studies. XXIII. Passivity of the Sn75-Zn alloy", M. Prazak, Collection Czechoslov. Chem. Communs. 25, 1126-31 (1960).

"Anode passivation of zinc in alkaline solutions", T. I. Popova, V. S. Bagotskii, nd B. N. Kabanov, Doklady Akad. Nauk. S.S.S.R., 132, 639-42 (1960).

"Anodic behavior of tin and zinc in alkaline electrolytes", M. E. Prostakov, A. I. Levin, and V. P. Kochergin, Zhur. Fiz. Khim. 35, 420-5 (1961).

"A radiotracer study of the passivation of zinc in chromate solutions. I.", K. G. McLaren, J. H. Green, and A. H. Kingsbury, Corrosion Sci. 1, 161-9 (1961).

"The zinc passivation theory and the possibility of the transformation of adsorbed passivating films in thick layers", B. N. Kabanov, Electro-chim. Acta 6, Nos. 1-4, 253-7 (1962).

"The theory of zinc passivation", B. N. Kavanov, Izv. Akad. Nauk. S.S.S.R., Otd. Khim. Nauk 1962, 980-3.

"Anodic passivation of zinc in alkali. I. Measurements at constant current densities", T. I. Popova, V. S. Bagotskii, and B. N. Kabanov, Zh. Fiz. Khim. 36, 1432-8 (1962).

"Anodic oxidation of zinc in alkaline solutions", H. Bartels and R. Landsberg, Z. Physik. Chem. <u>222</u>, 217-39 (1963).

"Anodic oxidation of the zinc-cadmium alloys in solutions of caustic soda", I. P. Dezider' eva nd L. F. Bychkova, Anodnaya Zashchita Metal., Kasansk. Aviats. Inst., Dokl. 1-oi (Pervoi) Mezhvuz. Konf. <u>1964</u>, 412-20.

"The passivation of vertical zinc anodes in potassium hydroxide solution", N. A. Hampson, M. J. Tarbox, J. T. Lilley and J. P. G. Farr, Electrochem. Technol. <u>2</u>, 11-12, 309-13 (1964).

"Voltamperometric study of anodic polarization of zinc in aqueous solutions", G. S. Vozdvizhenskii and E. D. Kochman, Anodnaya Zashchita Metal., Kazansk, Aviats. Inst., Dokl. 1-oi (Pervoi) Mezhvuz, Konf. <u>1964</u>, 360-75.

"The passivity of zinc in aqueous solutions of sodium carbonate and sodium bicarbonate", H. Kaesche, Electrochim. Acta. <u>9</u>(4), 383-94 (1964).

Iron

"The electrolytic and chemical passivation and activation of iron ", K. F. Bonhoeffer and U. F. Franck, Z. Elektrochem. <u>55</u>, 180-4 (1951).

"The activation spreading on passive iron electrodes", U. F. Franck, Z. Elektrochem. <u>55</u>, 154-60 (1951).

"Corrosion, passivity, and passivation of iron - the roles of pH and potential", M. Pourbaix, Soc. roy. belge ing. et ind., Mem. <u>1951</u>, No. 1, 40 pp.

"Passivation of iron in the presence of chlorides", M. Pourbaix and J. Feron, Compt. rend. reunion comite thermodynam. et cinet. electrochim. <u>1951</u>, 135-40 (Pub. 1952).

"Passivation and activation potential of iron. Cathodic corrosion of iron in the presence of oxygen", M. Pourbaix and J. Feron, Compt. rend. reunion comite thermodynam. et cinet. electrochim. <u>1951</u>, 128-34 (Pub. 1952).

"The nature of the films formed by passivation of iron with solutions of sodium phosphate", M. J. Pryor, M. Cohen, and F. Brown, J. Electrochem. Soc. 99, 542-5 (1952).

"Resistance of low nickel-high chromium-iron alloys containing molybedenum and copper to attack of sulfuric acid", W. Tofaute and H. J. Rocha, Inst. hierro acero 5, 80t-7 (Jan. 1952).

"Anodic polarization of passive and nonpassive chromium-iron alloys", H. H. Uhlig and G. E. Woodside, J. Phys. Chem. 57, 280-3 (1953).

"Passivity of iron", K. F. Bonhoeffer, Z. Metallkunde 44, 77-81 (1953)

"The anodic behavior of iron-chromium alloys in sulfuric acid solution", S. Morioka and K. Sakiyama, Technol. Repts. Tohoku Univ. 17, No. 2, 176-89 (1953).

"Passivity of iron", T. G. O. Berg, Z. Metallkunde 44, 82 (1953)

"Anodic passivation of iron in concentrated sulfuric acid", V. M. Novakovskii and A. I. Levin, Doklady Akad. Nauk S.S.S.R. 99, 129-32 (1954).

"The electrochemical behavior of iron in hot concentrated alkali solutions. I.", V. V. Losev and B. N. Kabanov, Zhur. Fiz. Khim. 28, 824-36 (1954).

"The break-down potential of passive iron-chromium alloys in sulfate solutions", G. Masing. T. Heumann, and H. Jesper, Arch. Eisenhuttenw. 25, 169-80 (1954).

"Electrochemical properties of alloys. III. Effects of hydrogen and chloride ions on anodic behavior of iron-chromium alloys in sulfuric acid solution", S. Morioka and K. Sakiyama, Nippin Kinzoku Gakkaishi 18, 643-6 (1954).

"The corrosion of passive iron in acid solution", K. J. Vetter. Z. Elektrochem. 59, 67-72 (1955).

"Kinetics of anodic passivation of iron. II. Solutions containing oxalic acid or sodium oxalate", S. F. Matas and M. S. Ribera, Anales real soc.espan. fis v guim (Madrid) 51B, 395-400 (1955).

"The activation potentials of iron-chromium alloys and their relations to the chemical stability in sulfuric acid", H. J. Rocha and G. Lennartz, Arch. Eisenhuttenw 26, 117-23 (1955).

"Oscillographic investigation of anodic behavior of iron in sodium hydroxide solutions", F. F. Faizullin, E. D. Kochman, and A. I. Turashev, Uchenye Zapiski Kazan. Gosudarst. Univ. im. V. I. Ul' yanova-Lenina, Obshcheuniv. Sbornik 116, No. 5, 77-81 (1956).

"Electrochemistry and corrosion", M. Pourbaix, Corrosion et anti-corrosion 5, 230-40, 286-93 (1957).

"The passivity of iron in acid solutions", A. M. Sukhotin and K. M. Kartasheva, Zhur. Fiz. Khim. 31, 1256-65 (1957).

"Interpretation of passivity, and especially of the Flade standard potential, of iron", H. Gohr and E. Lange, Z. Elektrochem. 61, 1291-1301 (1957).

"Iron passivity in hot concentrated solutions of alkalies", A. M. Sukhotin and K. M. Kartashova, Khur. Fiz. Khim. 32, 2068-72 (1958).

"Importance of the Flade potential for the passivity of iron in alkaline solutions", K. E. Heusler, K. G. Weil, and K. F. Bonhoeffer, Z. Physik. Chem. 15, 149-61 (1958).

"Experimental findings in passive iron", K. G. Weil, Z. Elektrochem. 62, 638-41 (1958).

"The passivity of iron in acid solutions. II.", A. M. Sukhotin and K. M. Kartasheva, Zhur. Fiz. Khim. 32, 1632-7 (1958).

"Study of the passive iron electrode by measuring its capacitance by the dynamic method", A. M. Sukhotin and K. M. Kartashova, Zhur. Fiz. Khim. 33, 2649-51 (1959).

"Corrosion of iron in nitric acid solutions under cathodic and anodic polarization", I. V. Oknin, Trudy Moskov. Inst. Khim. Mashinostroeniya 22, 7-39 (1960).

"Behavior of iron and steel in oxidizing solutions", N. D. Tomashov, N. P. Zhuk, and E. N. Mirolyubov, Proizv. i Obrabotka Stali i Splavov, Mosk. Inst. Stali, Sb. 1960, 39, 438-49.

"Electrochemical behavior of metals during anodic and chemical passivation in electrolytic solutions", Y. M. Kolotyrkin Intern. Congr. Metallic Corrosion, 1st, London, Engl. 1961, 10-20 (Pub. 1962).

"Anodic passivation of steel in concentrated alkali solutions by a galvanic current of an Fe-Ni couple", A. A. Sharnin and K. N. Shabalin, Zh. Fiz. Khim. 36, 209-13 (1962).

"Anodic behavior of iron at high potentials in solutions containing chloride ions", A. Rius and R. Lizarbe, Electrochim. Acta 7, 513-22 (1962).

"The mechanism of passivation processes on iron", W. T. Denholm, J. Australian Inst. Metals 7, 141-52 (1962).

"Flade Potential of iron in acid solution", K. J. Vetter and G. Klein, Z. Physik Chem. 31, 405-14 (1962).

"Potentiokinetic study of passivity phenomena in iron and steels with simultaneous microscope observations", M. Froment, Ph. Morel, and I. Epelboin, Mem. Sci. Rev. Met. 59, 225-32 (1962).

"Passivity of iron in alkaline solution", J. Tousek, Collection Czeh. Chem. Commun. 28, 2843-48 (1963).

"Influence of film thickness on the thermodynamic properties of thin oxide layers on iron", K. G. Weil, J. Electrochem. Soc. 110(6), 640-4 (1963).

"Nature of anodic passive and barrier coatings. I. Effect of chloride ions on the anodic behavior of iron in alkaline solutions", K. Schwabe, J. Electrochem. Soc. 110(6), 663-7 (1963).

"Anodic behavior of iron in alkaline solutions", T. Hurlen, Electrochim. Acta 10, 60-919(1963).

"The anodic oxidation of iron in a neutral solution. II. Effect of ferrous ion and pH on the behavior of passive iron", M. Nagayama and M. Cohen, J. Electrochem. Soc. 110, 670-80 (1963).

"Passivation characteristics of Fe-based alloys", G. M. Florianovich and Ya. M. Kolotyrkin, Dokl. Akad. Nauk S. S. S. R. 151, (1), 144-7 (1963).

"Potential/pH diagram for iron in sulfide-bearing media", J. Bouet and J. P. Brenet, Corrosion Sci. 3(1), 51-63 (1963).

"Depassivating action of halogen ions on Fe-base alloys", Ya. M. Kolotyrkin, G. V. Golovina, and G. M. Florianovich, Dokl. Akad, Nauk S. S. S. R. 148, 1106-9 (1963).

"Passivity of cast iron in alkaline solutions", J. Tousek, Collection Czech. Chem. Commun. 28, 1273-9 (1963).

"Optical studies of the formation and breakdown of passive films formed on iron single crystal surfaces in inorganic inhibitor solutions", J. Kruger, J. Electrochem. Soc. 110, 654-63 (1963).

"Mechanism of corrosion of iron in sulfide media", J. Bouet, Compt. Rend. 256, 1973-5 (1963).

"Anodic dissolution of iron. II. Passivation of iron in n utral HOAc-NaOAc solns", H. Nord. , C. E. Foverskov, and G. Bech Niels , Acta Chem. Scand. 18(3), 681-9 (1964).

"Thermodynamic relations relative to the passivity of iron", T. Markovic, Werkstoffe Korrosion 15(7), 543-50 (1964).

"Sulfates in the passive iron layer", O. L. Riggs, Jr. , Corrosion, 20(9), 275t-281t (1964).

"Anode passivation of Fe in alkali solutions", F. F. Faizullin and G. N. Mansurov, Anodnaya Zashchita Metal. , Kazansk, Aviats. Inst. , Dokl. 1-oi (Pervoi) Mezhvuz. Konf. 1964, 472-82.

Nickel

"Electrochemical properties of nickel", Yu. V. Baimakov and L. M. Evlannikov, Zhur. Fiz. Khim. 25, 483-94 (1951).

"Anode polarization effects of nickel in sulfuric acid", D. R. Turner, J. Electrochem. Soc. 98, 434-42 (1951).

"The anodic behavior of nickel", I. G. Trümpler and Hch. Meyer, Helv. Chim. Acta 35, 1304-10 (1952).

"The anodic behavior of nickel in sulfuric acid", R. Landsberg and M. Hollnagel, Z. Electrochem. 58, 680-5 (1954).

"Passivity phenomena with nickel", K. Hauffe and I. Pfeiffer, Z. Metallkunde 45, 554-62 (1954).

"The passivation and passivity of nickel. I. Aqueous solution", R. Piontelli and G. Serravalle, Z. Elektrochem. 62, 759 72 (1958).

"Anodic behavior of nickel. I. Effect of components of electrolyte", N. F. Murphy and O. C. Baharat, Bull. Virginia Polytech. Inst., Eng. Expt. Sta. Ser. No. 125, 18 pp. (1958).

"Passivation of nickel in acid solution - higher oxide film theory", G. Okamoto and N. Sato, Nippon Kinzoku Gakkaishi 24, 105-9 (1960).

"Mechanism of the anodic passivation of nickel in acid solution. Higher-valence oxide-film theory", N. Sato and G. Okamoto, Trans. Japan Inst. Metals 2, 113-19 (1961).

"Effect of halide ions on the passivity of nickel. II", G. Truempler and R. Keller, Helv. Chim. Acta 44, 1785-93 (1961).

"Mechanism of action of certain oxidizing agents inhibiting the corrosion of nickel and iron-chromium alloys", Ya. M. Kolotyrkin, N. Ya. Bune, and G. M. Florianovich, Ann. Univ. Ferrara Sez. 5, Suppl. 1960, 493-509 (Pub. 1961).

"Kinetics of the reduction of passivation layers on nickel by chloride", K. Schwabe and R. Radeglia, Werkstoffe Korrosion 13, 281-4 (1962).

"Anodic passivation of nickel in sulfuric acid solutions", N. Sato and G. Okamoto, J. Electrochem. Soc. 110, 605-14 (1963).

"The passivity of nickel", E. Kunze and K. Schwabe, Corrosion Sci. 4, 109-36 (1964).

"Influence of pH on corrosion and passivation of nickel", D. E. Davies, Corrosion 20(2), 47t-53t (1964).

Cadmium

"The electrochemical properties of cadmium in alkaline solutions",
S. A. Rozentsveig, B. V. Ershler, E. L. Shtrum, and M. M. Ostanina,
Trudy Soveshchaniya Elektrokhim. Akad. Nauk S. S. S. R. Otdel Khim.
Nauk 1950, 258-75 (1953).

"Anode polarization of cadmium in sodium hydroxide solutions", I. P.
Dezider'eva and N. E. Timoshenko, Uchenye Zapiski Kazan. Univ.
116, No. 1, 158-61 (1955).

"Oxidizability of powdered cadmium during its production by electrolytic
method", D. N. Gritsan, A. M. Bulgakova, and N. N. Ovcharenko,
Uchenye Zapiski Kharkov. Univ. 15, 53-8 (1956); Referat. Zhur., Met.
1957, Abstr. No. 21173.

"Anodic and cathodic polarization of amalgams. IV. Passivation of
cadmium and cadmium-zinc amalgams in alkaline solutions", A. M.
Shams El-Din, S. E. Khalafalla, and Y. A. El-Tantawy, J. Phys. Chem.
65, 1484-9 (1961).

"Polarization studies on cadmium by galvanostatic and potentiostatic
techniques", I. Sanghi, S. Visvanathan, and S. Ananthanarayanan,
Electrochim. Acta 3, 65-74 (1960).

"Chemical behavior of metallic single crystals", F. DeCarli, U. S.
Dept. Com., Office Tech. Serv., AD 278, 461, 23 pp. (1962).

"Anodic oxidation of cadmium in concentrated solutions of alkali",
A. L. L'vov and A. V. Fortunatov, Anodnaya Zashchita Metal., Kazansk.
Aviats. Inst., Dokl. 1-oi (Pervoi) Mezhvuz. Konf. 1964, 395-411.

Magnesium

"Protection of magnesium alloys", W. F. Higgins, Electroplating 3,
No. 8, 287-91 (1950).

"Passivation and activation of magnesium in alkali (potassium hydroxide)
solutions", E. V. Barelko and B. N. Kabanov, Doklady Akad. Nauk S. S. S. R.
90, 1059-62 (1953).

"The anodic behavior of aluminum and aluminum-magnesium alloys in sulfuric acid and sodium sulfate solutions", W. Machu and M. K. Hussein, Werkstoffe u. Korrosion 5, 49-54 (1954).

"The action of alkaline solutions on aluminum and aluminum alloys", W. Machu and M. K. Hussein, Werkstoffe u. Korrosion 5, 295-301 (1954).

"Corrosion of magnesium. II:", G. Wada, J. Chem. Soc. Japan, Pure Chem. Sect. 75, 276-9 (1954).

"Protection of magnesium alloys by inorganic films", M. A. Timonova, Korroziya i Zashchita Metal., Sbornik 1957, 311-27.

"Corrosion of magnesium alloys containing iron and nickel", J. H. Greenblatt, J. Appl. Chem. (London) 9, 401-5 (1959).

"Anode behavior of magnesium in some salt solutions in the presence of alkali", S. N. Pobedinskii and L. L. Kuz'min, Izv. Vysshikh Uchebn. Zavedenii, Khim. i. Khim. Tekhnol. 5, 954-9 (1962).

"Magnesium as a passive metal", P. F. King, J. Electrochem. Soc. 110(11), 1113-16 (1963).

"Protective properties of fluoride silicate films on magnesium", A. V. Solov'ev, Zh. Prikl. Khim. 36(11), 2547-50 (1963).

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The operation of primary, reserve batteries in a passive mode was explored. An anode can be put into the passive state by an appropriate electrical pulse and can be maintained in this condition by suitable connection to the positive battery electrode. Activation can be achieved by a cathodic electrical pulse.

The most promising systems for use as passive anodes were Zn-Co and Zn-Ni alloys. Zinc itself shows a characteristic active-passive transition, but the passive current is too high for use in the passive reserve mode. Alloys 78 Zn - 22 Co and 80 Zn - 20 Ni have acceptably high critical currents and low passive currents. However, at best, the passive current is still about $5 \mu A/cm^2$.

A comparison of primary reserve batteries operated in the passive mode with batteries activated by conventional gas generators shows that the passive current must be less than $1 \mu A/cm^2$ for the passive battery to be competitive. Preferably the passive current should be less than $0.1 \mu A/cm^2$.

14.		LINK A		LINK B		LINK C	
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